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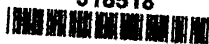
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# JOURNAL

OF

## THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN  
BRITISH AND FOREIGN JOURNALS.

### PART II.

#### General and Physical Chemistry.

**Influence of Halogens on the Optical Values of Double Bonds.** By G. CARRARA (*Gazzetta*, 23, ii, 1—7).—The author is determining the refraction constants of a number of unsaturated aliphatic halogen derivatives, with the object of finding an explanation of the anomalous refraction of such substances as dibromacetylene and tribromomethylene. In the present paper he gives the following measurements of the refractive powers of monobromomethylene and iso- $\alpha$ -bromopropylene.

*Monobromomethylene*.—Sp. gr. at  $4^{\circ}/4^{\circ} = 1.56558$ ;  $\mu_{H_a} = 1.44276$ ;  $\mu_D = 1.44622$ ;  $\mu_{H_\beta} = 1.45496$ ;  $\mu_{H_\gamma} = 1.46251$ ;

$$\frac{P(\mu_{H_a} - 1)}{d} = 30.26. \quad \frac{P(\mu_{H_a}^2 - 1)}{d(\mu_{H_a}^2 + 2)} = 18.10.$$

*Iso- $\alpha$ -bromopropylene*.—Sp. gr. at  $14.6^{\circ}/4^{\circ} = 1.43227$ ;  $\mu_{H_a} = 1.45189$ ;  $\mu_D = 1.45536$ ;  $\mu_{H_\beta} = 1.46374$ ;  $\mu_{H_\gamma} = 1.47082$ ;

$$\frac{P(\mu_{H_a} - 1)}{d} = 38.18. \quad \frac{P(\mu_{H_a}^2 - 1)}{d(\mu_{H_a}^2 + 2)} = 22.82.$$

The differences between the observed and theoretical values, calculating both for saturated and unsaturated compounds, are considerable, varying from 0.5 to 1.4 units,

W. J. P.

# ABSTRACTS OF CHEMICAL PAPERS.

**Abnormal Increase in the Refractive Power of Aromatic Bases.** By F. ZECCHINI (*Gazzetta*, 23, ii, 42—46).—The author has measured the refractive powers of diphenylamine and triphenylamine in benzene solution for the line  $N_{D_{25}}$ ; the values obtained are very high, and give abnormally high values for the atomic refraction of nitrogen. The results are summarised in the following table, and compared with those obtained for aniline by Gladstone; it is noteworthy that the latter observer found that the atomic refraction of nitrogen in the homologous derivatives of aniline increased as the series was ascended.

Substance.	$\frac{\mu_D - 1}{d}$ .	$P \frac{\mu_D^2 - 1}{(\mu_D^2 + 2)d}$ .	Atomic refraction of nitrogen.	
			From $\mu_D$ .	From $\mu_D^2$ .
$NH_2Ph$ .....	53·37	30·56	7·46	3·38
$NHPh_2$ .....	102·04	57·62	14·56	6·41
$NPh_3$ .....	149·40	84·46	20·49	9·22

The measurements were made at 11—14°, and in solutions containing 9—17 per cent. of the bases. W. J. P.

**Cause of the Variation of the Rotatory Power of the Solutions of certain Optically Active Substances. Rotatory Power of Amorphous Substances.** By A. BÉCHAMP (*Bull. Soc. Chim.*, [3], 9, 511—529).—It is well known that when glucose crystallised in nodules is dissolved in water, the rotatory power of the solution gradually diminishes, at last becoming little more than half its initial value. The author finds that glucose crystallised in nodules, and obtained by the saccharification of starch, contains a small quantity of dextrin insoluble in alcohol of 93°, and with a high rotatory power,  $[\alpha]_D = +125^\circ$ ; after this is removed, the alcoholic solution gradually deposits glucose in groups of small crystals with distinct faces. These have the composition  $C_6H_{12}O_6 + H_2O$ , and when dissolved in water the initial rotatory power is  $[\alpha]_D = +96·4^\circ$ ; but the rotatory power gradually diminishes, and after 24 hours becomes constant with the value  $[\alpha]_D = +52·04^\circ$ . If these values are calculated to anhydrous, instead of to hydrated, glucose, they become respectively  $+106·04^\circ$  and  $+57·23^\circ$ .

If the hydrated glucose is dried at 100°, and then dissolved in water, the solution has at once the rotatory power  $[\alpha]_D = +57·6^\circ$ . If also after the rotatory power of a solution of hydrated glucose has become constant, the liquid is evaporated, and the residue is dissolved in water, the rotatory power is likewise  $+57^\circ$ . It would seem, therefore, that the initial rotatory power of the solution of crystallised glucose is due to the hydrate, whilst the final value is due to anhydrous glucose, dehydration having taken place in solution.

If the crystallised glucose is heated in a current of dry air at about 60°, dehydration takes place without fusion as at 100°; but, never-

theless, when the anhydrous glucose is dissolved in water, the rotatory power has the higher value, and only becomes  $+57^\circ$  after some time. It would seem, therefore, that although crystallised glucose is not birotatory, anhydrous glucose has this property, and exists in two distinct modifications.

Glucose dehydrated with fusion at  $100^\circ$ , or obtained by evaporation of a solution with the rotatory power  $+57^\circ$ , melts at  $100^\circ$ , and is a soft and truly amorphous mass which absorbs moisture from the air, and cannot be crystallised, whereas glucose dehydrated without fusion does not melt at  $100^\circ$ , remains hard, retains its crystalline appearance, and absorbs moisture from the air without deliquescence, again producing the hydrate,  $C_6H_{12}O_6 + H_2O$ . In fact, if water is added to the dehydrated substance, combination takes place with development of heat. It follows that the higher rotatory power observed is due to the hydrate.

The rotatory power  $+57^\circ$  is due to anhydrous glucose which exists in the solution in an amorphous form, and it follows that optical activity is not necessarily connected with crystalline form.

The author suggests that, as a rule, compounds exist in both an amorphous and a crystalline form, although in many cases the crystalline modification is very difficult to obtain, and only the amorphous form is known. Amongst the latter may be mentioned the amyloses, cellulose, proteids, &c.

The potassium compound of soluble starch has immediately after dissolution a rotatory power of  $[\alpha]_D = +188.3^\circ$ , but if the solution is gradually diluted, the rotatory power increases, and tends to approach that of soluble starch itself,  $+212^\circ$ . The potassium compound dissociates as the degree of dilution increases, but both it and the soluble starch are amorphous.

As examples of other substances that are unquestionably amorphous as usually obtained, the author mentions lignodextrin, obtained by the action of hydrochloric acid on cellulose; viscose, from saccharose,  $[\alpha]_D = +224^\circ$ ; ossein, dissolved in hydrochloric acid,  $[\alpha]_D = -411.6^\circ$ ; ossein soluble in water,  $[\alpha]_D = -359.6$  at  $11^\circ$ , but varying greatly with the temperature, and becoming only  $-168^\circ$  to  $-177^\circ$  at  $30^\circ$ ; gelatin, soluble "cartilagein," the products of the gastric digestion of ossein and gelatin. It is noteworthy that the rotatory power of almost all these solutions diminishes very considerably as the temperature rises.

A solution of very active diastase gave a rotatory power of  $[\alpha]_D = -114.1^\circ$ , and this remained the same after boiling, although the diastatic power had been destroyed. In a similar manner, a solution of zythozymase retains its optical activity after boiling, although it has lost its power of fermenting saccharose.

It seems clear, therefore, that many substances which have never been crystallised have a marked optical activity; but this is not observed in solution only, for a film of gelatin has a marked rotatory power.

Optical activity is not necessarily connected with crystalline form, but depends chiefly on the chemical constitution of the molecules of the active substances.

G. H. B.



**Chemical Potential of Metals.** By W. D. BANCROFT (*Zeit. physikal. Chem.*, 12, 289—297).—The author has investigated the difference of potential between the metals magnesium, zinc, cadmium, tin, lead, bismuth, mercury, and platinum in various salt solutions. He finds that when the pairs of metals are selected from magnesium, zinc, cadmium, tin, lead, and bismuth, neither the positive nor the negative ion of the salt solution has any effect on the electromotive force, which also remains constant although the dilution varies from 10 to 1000 litres. When mercury forms one pole of the combination, the influence of the negative ion of the salt solution is very marked, but concentration does not influence the electromotive force. In the case of platinum, the difference of potential depends on the concentration of the salt solution when the dissolved salt is a haloid. This is possibly due to the tendency of platinum to form platinochlorides, &c., in which the platinum is not present as an ion.

It would appear, although the numerical agreement still leaves something to be desired, that the electromotive force of the combination  $M_1 | RX | M_2$  is identical with that of the reversible combination  $M_1 | M_1X | M_2X | M_2$ . J. W.

**Electromotive Forces of Polarisation. Part II.** By M. LE BIANC (*Zeit. physikal. Chem.*, 12, 333—358; compare Abstr., 1891, 1405).—From a further study of the electromotive forces of polarisation in salt solutions, the author finds that at the decomposition point in a solution from which a metal is deposited on the cathode, the electromotive force of polarisation at this electrode is equal to the electrolytic solution pressure of the metal in the solution, and is independent of the nature of the electrode, provided it is not attacked. The numerous apparent exceptions to this simple rule are referred by him to the development of gases at the electrodes, in which case the electromotive force necessary for their liberation depends in great measure on the nature and condition of the electrodes employed. By suitable arrangement of his apparatus, he was able to show that in many of these cases the solutions exhibited the normal behaviour, and that the electrolytic decomposition and formation of water (by means of a gas battery) is a reversible process. Salts of zinc, cobalt, nickel, and cadmium have a high decomposition point, and usually deposit the metal without evolution of hydrogen. This behaviour is due to special circumstances, and it is shown that under appropriate conditions hydrogen appears at the cathode, and not the metal.

The assumption that the atoms of gases contain a greater amount of energy than the molecules is considered by the author to be untenable. They form two states of matter with practically the same energy content, the difference between them being that the atoms enter into chemical action with a great velocity of reaction, which is only approached by the molecules when a catalyst is present.

J. W.

**Electromotive Forces of Insoluble and Complex Salts.** By K. ZENGELIS (*Zeit. physikal. Chem.*, 12, 298—313).—Ostwald obtained results for silver salts in agreement with the following general prin-

ciples:—Insoluble and complex salts, on account of the small concentration of their metallic ions, show considerable deviations from the calculated value of the electromotive force of two-fluid combinations in which they occur, the deviation increasing with the decreasing solubility of the salt. Salts soluble in the complex compounds have a smaller deviation, and salts insoluble in them a greater deviation, than the complex compounds themselves. The author has tested the validity of these rules, in the case of a number of slightly soluble and complex compounds of silver, copper, lead, nickel, and cobalt, and has obtained results in harmony with them.

In the case of the phosphates of lead, cadmium, and silver, the electromotive force gradually diminishes on standing, owing probably to the formation of basic salts. Similar diminutions were observed with the carbonates, and to a smaller extent with the arsenates. Where no basic salt is formed, as in the case of silver carbonate, the electromotive force remains constant. With sulphides, an increase of the electromotive force was sometimes noticed, probably due to the transformation of the hydrosulphides at first formed into normal sulphides.

J. W.

**Secondary Heats of Galvanic Elements.** By H. JAHN (*Ann. Phys. Chem.*, 50, 189—192).—The author gives the following corrected numbers for secondary heats of galvanic elements.

Element.	Secondary heat.	
	Found.	Calculated.
	Cal.	Cal.
Cu, Cu(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>    Pb(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> , Pb.....	-4.151	-4.784
Ag, AgCl    ZnCl <sub>2</sub> + 100H <sub>2</sub> O, Zn.....	+5.139	+5.082
Ag, AgCl    ZnCl <sub>2</sub> + 50H <sub>2</sub> O, Zn.....	+2.620	+2.609
Ag, AgCl    ZnCl <sub>2</sub> + 25H <sub>2</sub> O, Zn.....	+2.654	+2.51
Ag, AgBr    ZnBr <sub>2</sub> + 25H <sub>2</sub> O, Zn.....	+1.488	+1.326

He also replies to some objections raised by Streintz (*Ann. Phys. Chem.*, [2], 49, 564) as to his method.

J. W.

**Properties of Mixtures of Amines and Acids.** By D. KONOVALOFF (*Ann. Phys. Chem.*, [2], 49, 733—760).—In this paper, the author studies the electrolytic conductivity, freezing point, heat of solution, heat of dilution, and specific heat of mixtures of feeble bases, such as aniline and acids of the acetic series. An account of most of his conductivity experiments has already been published (compare *Abstr.*, 1893, ii, 356). He formulates his conclusions as follows:—

1. Solutions formed by amines and organic acids are conductors of about the same order as solutions of organic acids in water.

2. At a high, but not infinite, dilution the conductivity of the solutions becomes infinitely small.

3. The curves which represent the electrical conductivity of these

solutions as dependent on the percentage composition, are not symmetrical. The maximum lies on the side of the liquid with smaller molecular weight and volume, and to an extent which is determined by the differences between the molecular weights (and the molecular volumes) of the two liquids.

4. The curves near the  $x$ -axis are mostly concave, and the concavity is greater, as the molecular weight and volume of the dissolved substance in comparison with those of the solvent is greater.

5. The peculiar behaviour of aqueous solutions appears to be due principally to the small molecular weight and volume of the solvent.

6. The conductivity curves for mixtures of aniline and acetic acid exhibit a series of singular points, corresponding with solutions of simple multiple proportions.

7. The conductivity of liquids at the ordinary temperature is called into play by chemical affinity between the dissolved electrolyte and the excess of the solvent. The special condition of the unstable compounds thus brought into existence favours chemical transformation, without which no electrolytic conductivity is possible.

The curves for the heats of solution against percentage composition have maxima which in no case corresponds with the ratio of 1 mol. acid to 1 mol. amine, but is always on the side of the solutions with excess of acid. The heat of dilution of the solution by the acid is always positive, whilst, with an amine as the diluent, heat is developed up to a certain point, after which it is absorbed.

The depression of the freezing point of acetic acid by aniline is normal for dilute solutions.

J. W.

**Melting Points of Inorganic Salts.** By V. MEYER and W. RIDDLE (*Ber.*, 26, 2443—2451).—The authors have commenced this work in the hope of finding relations between the melting points of inorganic salts similar to those known to exist between the melting points of organic compounds.

The method employed consists in melting the salt in a platinum crucible, and determining the solidifying point, by means of the platinum air-thermometer described by V. Meyer and Freyer. Test experiments with tin, lead, zinc, naphthalene, and anthraquinone gave correct numbers.

At present the following melting points have been observed:—Sodium chloride, 851°; sodium bromide, 727°; sodium iodide, 650°; potassium chloride, 766°; potassium bromide, 715°; potassium iodide, 623°; potassium carbonate, 1045°; sodium carbonate, 1098°; borax, 878°; sodium sulphate, 843°; potassium sulphate, 1073°.

E. C. R.

**Molecular Volumes of Boron Compounds.** By A. GHIRA (*Gazzetta*, 23, ii, 8—11).—The author has determined the molecular volumes of a number of liquid compounds of boron; the results are given in the following table (p. 7).

The molecular volumes of water, given in column 4, are calculated from the values concerned in the reaction by which the boron compounds are obtained. Twice the observed molecular volume of the substance is subtracted from the sum of boric anhydride, and six times the

# GENERAL AND PHYSICAL CHEMISTRY.

Substance.	$d$ at 4°.	Mol. volume at 0°.	Mol. volume of water.
$\text{BCl}_3$ .....	1.43386	81.94	—
$\text{BBr}_3$ .....	2.64985	94.72	—
$\text{B}(\text{OEt})_3$ .....	0.88683	164.72	17.0
$\text{B}(\text{OC}_4\text{H}_9^\beta)_3$ .....	0.86437	266.09	16.6
$\text{B}(\text{OC}_5\text{H}_{11}^\beta)_3$ .....	0.87112	312.24	17.8
$\text{B}(\text{OC}_3\text{H}_5)_3$ .....	0.94209	193.19	17.2

molecular volume of the alcohol used in the preparation; this difference, divided by three, gives the molecular weight of water. The agreement is thus seen to be satisfactory. The molecular volumes of consecutive members of the homologous series differ by about 16 units for each increment of  $\text{CH}_2$ , as has been shown for other series by Horstmann (Abstr., 1886, 750).

W. J. P.

**Electrolytic Determination of the Solubility of Slightly Soluble Substances.** By F. KOHLRAUSCH and F. ROSE (*Ann. Phys.*

Salt.	Salt contained at 18° in 1 litre in		Approximate temperature co- efficient at 18°.
	Milligram equivalents.	Milligrams.	
Silver chloride .....	0.0117	1.7	0.052
" bromide .....	0.002	0.4	(0.023)
" iodide .....	0.0006	0.1	—
Mercurous chloride .....	0.013	3.1	0.049
Mercuric iodide .....	0.002	0.5	—
Cuprous iodide .....	0.04 ?	8.0 ?	—
Cuprous thiocyanate .....	0.004 ?	0.5 ?	—
Calcium sulphate .....	0.35	14.0	0.007
Barium sulphate .....	0.022	2.6	0.018
" " (heavyspar) ..	0.025	2.9	0.017
Strontium sulphate .....	1.18	107.0	0.000
Calcium sulphate .....	30.5	2070.0	0.003
Lead sulphate .....	0.30	46.0	0.007
Barium oxalate .....	0.66	74.0	0.021
Strontium oxalate .....	0.51	45.0	0.018
Calcium oxalate .....	0.092	5.9	0.016
Barium carbonate .....	0.24	24.0	0.013
Strontium carbonate .....	0.15	11.0	0.015
Calcium carbonate .....	0.26	13.0	0.008
" " (aragonite) ..	0.30	15.0	0.008
Lead carbonate .....	(0.025)	(3.0)	0.009
Silver chromate .....	0.17	23.0	0.032
Barium chromate .....	0.03	3.8	0.023
Lead chromate .....	0.001	0.2	—
Magnesium hydroxide .....	0.41	9.0	0.000

*Chem.*, [2], 50, 127—137; compare *Abstr.*, 1893, ii, 519).—The values given in the table, p. 7, for the solubility in water of so-called "insoluble" salts are calculated from determinations of the electric conductivity of the saturated solutions. J. W.

**Solubilities.** By A. ETARD (*Bull. Soc. Chim.*, [3], 9, 82—87).—The author regards the curve of solubility as the locus of the melting points of mixtures of the dissolved substance and the solvent (*Abstr.*, 1889, 460). In order to obtain the complete curve, the solubilities must be expressed, not as the amount of substance dissolved by 100 parts of the solvent, but as the amount contained in 100 parts of the saturated solution. The complete curve cannot, for obvious reasons, be obtained in the case of the majority of solutions of inorganic salts in water; and, therefore, the author has turned his attention to the solubilities of organic compounds in organic solvents. Complete solubility curves are given for several cases of this kind. Attempts were made, by the use of solvents melting at low temperatures, to obtain cases in which the solubility was ultimately reduced to zero, but without positive success. Chloroform (m. p.  $-65^{\circ}$ ) at  $-50^{\circ}$  still dissolves considerable quantities of naphthalene and triphenylmethane. In most cases, however, the different solubility curves converge at low temperatures into a single line, the direction of which is towards the ordinate zero at the melting point. H. C.

**The Colour of the Ions.** By J. WAGNER (*Zeit. physikal. Chem.*, 12, 314—321).—Magnanini (*Abstr.*, 1893, ii, 510) has stated that violuric acid when dissolved in pure water is colourless, and that the colour of its salts in aqueous solution cannot be attributed to a coloured negative ion. The author has repeated Magnanini's experiments with the acid, but has failed to obtain a colourless solution, water carefully freed from alkali always giving a violet liquid. He further finds that the absorption of solutions of the acid and the sodium salt is proportional to the number of violuric ions in the solution, as determined by the electrical conductivity. The absorption of the acid does not decrease proportionally to the dilution, as it should if the presence of a salt as impurity were the cause, but to the square root of the dilution, that is, proportionally to the number of negative ions. The decolorisation by means of other acids proceeds according to the law of isohydric solutions. A chromolithographic table of the colours of 16 solid violurates is given; these show great differences in colour, but when dissolved in water and sufficiently diluted, they all give violet solutions (due to the negative ion), provided the positive ion is colourless. J. W.

**Saline Solutions.** By C. CHARPY (*Ann. Chim. Phys.*, [6], 29, 1—68).—With a view of further elucidating the question as to the condition of a dissolved salt and its relation to the solvent, the author has determined, with all possible accuracy, the densities of a number of aqueous solutions of inorganic salts and organic acids of various concentrations. From these, the contraction was calculated, it having been already shown (*Abstr.*, 1892, 1146) that the density is a linear

function of the contraction. The coefficient of contraction is given by the equation

$$K = \frac{1}{D} \left( 1 + \frac{S}{D} \frac{dD}{dS} \right)$$

where  $S$  is the percentage composition of a solution of density  $D$ . The coefficient is always less than unity, so that dilution of a solution is always accompanied by a contraction. It diminishes with the concentration, so that a greater contraction is produced by diluting a concentrated than by diluting a dilute solution. It increases with the temperature, so that the contraction produced by dilution at a high temperature is smaller than that produced by dilution at a low one. If the concentration be expressed in terms of the ratio of the number of molecules of the dissolved compound to the number of molecules of the solvent, the curves representing the coefficient of contraction as a function of the concentration will take some simple form, and in any series of analogous compounds will be found arranged in the order of the magnitudes of the molecular weights. The last property is also characteristic of the curves obtained if the density is substituted for the coefficient of contraction. The curves in this case are linear in form, the density of a solution being a linear function of the concentration when the latter is expressed as above. This last result holds also for mixtures of salts in solution, and it is, therefore, possible to apply this law to the study of chemical equilibrium between salts in solution.

H. C.

**The Hydrate Theory.** By W. MEYERHOFFER (*Ber.*, 26, 2475—2478).—The author points out that the curves obtained by Pickering for the depression in freezing point in various solutions are in reality solubility curves, and reasons that since no breaks have hitherto been found in solubility curves unless the solid in equilibrium with the solution itself undergoes transformation, the breaks observed by Pickering have no real existence.

J. W.

**Equilibrium of Solutions with two and three Components.** By H. W. B. ROOZEBOOM (*Zeit. physikal. Chem.*, 12, 359—389).—The author gives a full theoretical discussion of the nature of the solubility curves for systems composed of two and of three components. An example of the equilibrium of a system of two components is to be found in the solubility relations of ferric chloride and its hydrates in water. Here the components are water and anhydrous ferric chloride; ice, the anhydrous salt, and the various hydrates form the solid phases, solutions of varying concentration forming the liquid phase. The solubility curves of the components are termed by the author side curves, the solubility curves of the hydrates (in this case *binary* compounds) being called intermediate curves. With systems of three components there may be *ternary* solid phases; for example, the hydrate of a double salt. The following tables exhibit the characteristic properties of the various curves and their points of intersection. The solid phases are denoted by  $S_1$ ,  $S_2$ , &c., the liquid phase (solution) by  $L$ .

*Characteristics of Solubility Curves.*

Nature of curve.	Solid phases.	Direction of endo- thermic transforma- tion at the maximum temperature of the curve.
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## A. Two Components.

Side.....	One simple .....	$S \rightarrow L$ .
Intermediate .....	One binary .....	$S \rightarrow L$ .

## B. Three Components.

Side .....	Two simple..... One simple + one binary... Two binary .....	$S_1 + S_2 \rightarrow L$ . $S_1 + S_2 \rightarrow L$ , or $S_1 \rightarrow L + S_2$ .
Intermediate .....	One simple + one binary Two binary <div style="display: inline-block; vertical-align: middle; margin-left: 10px;"> <math>\left\{ \begin{array}{l} \text{containing} \\ \text{together} \\ \text{all three} \\ \text{components} \end{array} \right\}</math> </div> One simple + one binary. One binary + one ternary Two ternary	$S_1 + S_2 \rightarrow L$ .  $\left\{ \begin{array}{l} S_1 + S_2 \rightarrow L, \\ \text{or} \\ S_1 \rightarrow L + S_2. \end{array} \right.$

*Points of Intersection.*

Intersecting curves.	The intersection is a temperature minimum for	Direction of endo- thermic transforma- tion at intersection.
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## A. Two Components.

Two side.....	Both curves .....	$S_1 + S_2 \rightarrow L$ .
One side and one interme- diate	Both curves, or .....	$S_1 + S_2 \rightarrow L$ .
Two intermediate .....	One curve .....	$S_1 \rightarrow L + S_2$ .

## B. Three Components.

Three side .....	Three curves .....	$S_1 + S_2 + S_3 \rightarrow L$ .
Two side and one interme- diate	Three curves, or.....	$S_1 + S_2 + S_3 \rightarrow L$ .
One side and two interme- diate	Two curves .....	$S_1 + S_2 \rightarrow L + S_3$ .
Three intermediate .....		

**Temperature of Explosion of Mixtures of Gases.** By V. MEYER and A. MÜNCH (*Ber.*, 26, 2421—2432).—The explosion was effected in a glass vessel, situated inside the bulb of an air thermometer, the latter being immersed in a metal bath. The mixture of a gas with the amount of oxygen theoretically necessary for its complete combustion was passed through a fine tube to the bottom of the glass vessel, and lighted as it issued from the mouth of the tube which formed the upper continuation of the vessel. At a certain temperature the flame ran down the tube, and the contents of the vessel exploded. This temperature—the temperature of explosion—was then determined by displacing the air contained in the air thermometer with hydrogen chloride, collecting it over water, and measuring it.

A series of experiments was first made with hydrogen and oxygen. The temperature of explosion is not constant, but varied in 38 experiments from about 620° to 680°, being about 650° in the mean. It is not affected by variations in the rapidity with which the gases enter the glass vessel, or by the presence of glass splinters or sand. The presence of platinum prevents an explosion, the gases combining quietly, and if the glass vessel is very small no explosion occurs.

Some experiments were then made with carbonic oxide and with hydrogen sulphide, but these gases, for the most part, combined quietly with oxygen.

The following aliphatic hydrocarbons were then examined, and found to have the following temperatures of explosion when mixed with oxygen. Methane, 656—678°; ethane, 605—622°; ethylene, 577—590°; acetylene, 509—515°; propane, 545—548°; propylene, 497—511°; isobutane, 545—550°; isobutylene, 537—548°; coal-gas (with three times its volume of oxygen), 647—649°. It would thus appear that the temperature of explosion falls as the number of carbon atoms in the molecule increases; that it is probably lower for primary than for the corresponding secondary hydrocarbons; and is less for hydrocarbons containing a double bond than for those containing only single bonds, and still less for those containing a triple bond.

C. F. B.

**Extraction Apparatus.** By J. TCHERNIAC (*Ber.*, 26, 2359).—A defence of the author's apparatus (*Abstr.*, 1893, i, 229) for extraction with hot ether against the objections urged by Hagemann (*ibid.*, ii, 567).

C. F. B.

## Inorganic Chemistry.

**Hydrates of Hydrogen Iodide.** By S. U. PICKERING (*Ber.*, 26, 2307—2310).—In continuation of his previous work on the hydrates of hydrogen chloride (*Proc.*, 1893, 45) and of hydrogen bromide (*Phil. Mag.*, 1893), the author has succeeded in isolating three



hydrates of hydrogen iodide. The *dihydrate*,  $\text{HI} \cdot 2\text{H}_2\text{O}$ , forms large crystals melting at about  $-43^\circ$ . The *trihydrate*,  $\text{HI} \cdot 3\text{H}_2\text{O}$ , melts at  $-48^\circ$ , and forms small, granular crystals. The *tetrahydrate*,  $\text{HI} \cdot 4\text{H}_2\text{O}$ , melts at  $-36.5^\circ$ , and is deposited in large, transparent, granular crystals.

The numerical results are tabulated, and are also represented graphically in the form of curves. The following hydrates of hydrogen chloride and of hydrogen bromide are known.  $\text{HCl} \cdot \text{H}_2\text{O}$ ;  $\text{HCl} \cdot 2\text{H}_2\text{O}$ , m. p.  $-17.4^\circ$ ;  $\text{HCl} \cdot 3\text{H}_2\text{O}$ , m. p.  $-24.8^\circ$ ;  $\text{HBr} \cdot \text{H}_2\text{O}$ ;  $\text{HBr} \cdot 2\text{H}_2\text{O}$ , m. p.  $-11.2^\circ$ ;  $\text{HBr} \cdot 3\text{H}_2\text{O}$ , m. p.  $-48^\circ$ ;  $\text{HBr} \cdot 4\text{H}_2\text{O}$ , m. p.  $-55.8^\circ$ . No simple relationship appears to exist between the melting points of the various hydrates of the three acids. J. B. T.

**Decomposition of Hydrogen Iodide by Heat.** By M. BODENSTEIN (*Ber.*, 26, 2603—2611; compare Abstr., 1893, ii, 369).—Further experiments have yielded the following numbers for the amount of hydrogen iodide decomposed at various temperatures.

290°	310°	320°	340°	350°	394°	448°	518°
0.164	0.167	0.160	0.171	0.176	0.196	0.214	0.236

A minimum appears to exist at  $320^\circ$ , at which temperature the heat of reaction is probably zero.

The influence of pressure is seen in the following table.

Pressure in atmospheres.	350°.	448°.	518°.
0.5	0.135	0.202	0.225
1.0	0.176	0.214	0.236
1.5	0.192	0.222	0.241
2.0	0.199	0.231	0.244

The constant C of the velocity equation for the decomposition varies as follows.

Pressure.	350°.	448°.
0.5	0.0000345	0.00266
1.0	0.0000699	0.00503
1.5	0.0001151	0.00820
2.0	0.0001571	0.01143

This table shows that the constant is very nearly proportional to the pressure. J. W.

**Action of Ammonia on some Peroxides.** By O. MICHEL and E. GRANDMOUGIN (*Ber.*, 26, 2565—2568).—When dry gaseous ammonia is passed over the heated peroxides of sodium, barium, manganese, and lead, the ammonia is oxidised to nitrogen, and the metal left either

as hydroxide (sodium and barium) or oxide (manganese sesquioxide, litharge). In addition to these products, in all cases except that of barium, a small amount of nitrous and nitric acids is formed.

A. H.

**Properties and Constitution of Hydroxylamine and its Homologues.** By W. BRÜHL (*Ber.*, 26, 2508—2520). See this vol., i, 9.

**Preparation of Nitrous Oxide.** By W. SMITH (*J. Soc. Chem. Ind.*, 11, 867—869; 12, 10—11).—A mixture of ammonium sulphate and sodium nitrate, kept at 215° for 2—3 hours, undergoes, in great part, decomposition into sodium sulphate and ammonium nitrate. If, however, it is rapidly raised to a higher temperature, nitrous oxide begins to be evolved at 230°, and comes off with some rapidity at 240—250°. During the heating up a little ammonia is evolved, and the longer the mixture is kept at about 220—230°, the more ammonia is lost. If, then, the two salts have been mixed in molecular proportions, the deficiency in the ammonia leads to the evolution of some of the higher oxides of nitrogen towards the end of the reaction. This may be remedied by increasing the proportion of ammonium sulphate, the mixture, with an additional 5 per cent. of that salt, affording a larger yield of nitrous oxide than would be obtained from the equivalent quantity of ammonium nitrate. The gas is evolved with regularity, whereas ammonium nitrate, raised to 240°, decomposes with a rapidity accelerating towards explosive violence. M. J. S.

**Hyponitrous acid.** By A. THUM (*Monatsh.*, 14, 294—310).—The author supports the theory of Dunstan and Dymond (*Trans.*, 1887, 656), according to which, the first product of the reduction of sodium nitrite in alkaline solution is the sodium derivative of a dihydroxylamine, two molecules of which then condense to form sodium hyponitrite, (1)  $\text{Na}_2 + 2\text{H}_2\text{O} + \text{NaNO}_2 = \text{NaN}(\text{OH})_2 + 2\text{NaOH}$ . (2)  $2\text{NaN}(\text{OH})_2 = \text{Na}_2\text{N}_2\text{O}_2 + 2\text{H}_2\text{O}$ . This condensation seems to be favoured by the presence of an excess of alkali, for if this be neutralised by a current of carbonic anhydride, no hyponitrite is formed. The nitrogen evolved during the reduction is not due to the reduction of hydroxylamine, to which it has usually been ascribed, for this substance is scarcely attacked by sodium amalgam, but probably to a reaction between the dihydroxylamine and hydroxylamine,  $\text{NH}_2\text{OH} + \text{NH}(\text{OH})_2 = \text{N}_2 + 3\text{H}_2\text{O}$ . The preparation of hyponitrites by means of ferrous hydroxide has no advantage over the ordinary method of reduction by means of sodium amalgam.

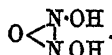
Hyponitrous acid is also formed by the action of hydroxylamine on nitrous acid. About 2 per cent. of the theoretical amount of the silver salt is formed when equivalent solutions of hydroxylamine hydrochloride or sulphate and sodium nitrite are mixed, allowed to remain until the violent evolution of nitrous oxide has ceased, and then treated with a solution of silver nitrate. No hyponitrite is formed in alkaline solution. Further investigations are in progress as to the exact course of this reaction. Attempts to isolate hyponitrous acid from the dry silver salt by means of dry hydrogen

sulphide showed that even at low temperatures it is very unstable and liable to explosive decomposition; the remaining experiments were, therefore, made with solutions of the acid, prepared by acting on the silver salt with the calculated amount of hydrochloric acid. The solution is colourless and strongly acid, and is stable towards dilute acids and alkalis even on boiling. On titration with potash, in the presence of phenolphthaleïn or litmus, the solution remains acid until the acid salt is formed, and then becomes alkaline. The acid does not affect methyl-orange, and does not expel carbonic anhydride from the alkali carbonates. In acid solution, it is quantitatively converted by potassium permanganate into nitric acid, whilst in alkaline solution, nitrous acid is formed. Pure solutions of the acid, contrary to the statements of Divers on the one hand, and Van der Plants on the other, do not decolorise solutions of iodine and prevent the formation of iodide of starch, neither do they liberate iodine from acid solutions of potassium iodide. Hyponitrous acid is very stable towards reducing agents, both in the presence of acids and alkalis. Solutions of the acid hyponitrites of the alkalis give precipitates with the salts of many metals. These metallic salts are being further examined.

*The Oxidation of Hydroxylamine.*—When hydroxylamine is acted on by alkaline permanganate, an amount of oxygen is taken up which is exactly half way between the amounts required to convert the hydroxylamine into hyponitrous acid on the one hand, and nitrous acid on the other. This corresponds with the formation of a substance of the formula  $\text{H}_2\text{N}_2\text{O}_3$ , which bears the same relation to hyponitrous acid that an azoxy- does to an azo-compound,



Hyponitrous acid (azohydroxyl).



Azoxyhydroxyl.

Experiments are in progress on the isolation of this substance. Hydroxylamine is also oxidised by mercuric oxide, cupric oxide, hydrogen peroxide, and alkaline potassium ferricyanide, small amounts of hyponitrite being formed in each case. The greater part of the nitrogen, however, is converted into nitrous oxide or nitrous acid.

A. H.

[The paper by W. Wislicenus (Abstr., 1893, ii, 311) in which the formation of hyponitrous acid by the interaction of hydroxylamine, and nitrous acid is described was read at a somewhat later date than the foregoing.]

A. H.

**Rate of Oxidation of Hydrogen Phosphide.** By H. J. VAN DE STADT (*Zeit. physikal. Chem.*, 12, 322—332).—When dry gaseous hydrogen phosphide and oxygen are brought together at a low pressure, they combine at once with emission of light to form phosphorous acid according to the equation  $2\text{PH}_3 + 3\text{O}_2 = 2\text{H}_3\text{PO}_3$ . The apparatus used by the author to determine the combining proportions consisted of a pear-shaped bulb connected on the one hand with an air-pump and manometer, and on the other with a gas pipette, by means of which definite quantities of gas could be introduced. The

bulb was rendered vacuum, a certain number of measures of hydrogen phosphide admitted, and then oxygen, measure by measure, until the flash on combination no longer appeared. The manometer showed no change of pressure before and after the reaction.

When the gases were admitted very slowly from the pipette, an intermittent greenish-blue light was observed, and the manometer indicated that equal volumes of oxygen and hydrogen phosphide interacted, leaving an equal volume of a permanent gas as residue. When the mixing of the two gases was allowed to take place by diffusion at a pressure under 50 mm., accurate results were obtained, and the crystalline solid which was deposited on the walls of the bulb was proved to be metaphosphorous acid, formed according to the equation  $\text{PH}_3 + \text{O}_2 = \text{H}_2 + \text{HPO}_2$ . The crystals melt above  $80^\circ$ , and deliquesce in presence of a little water vapour, the solution shortly afterwards becoming solid again from formation of orthophosphorous acid.

Slow oxidation at greater pressures appears to proceed approximately according to the equation  $4\text{PH}_3 + 5\text{O}_2 = 2\text{HPO}_2 + 2\text{H}_3\text{PO}_3 + 2\text{H}_2$ . Dilution does not increase the rate of oxidation continuously, but, when a certain low pressure is reached, explosion takes place suddenly. The limiting pressure for explosion depends very greatly on the amount of moisture present, which, in this case, retards and prevents the oxidation, a result in direct contrast with those obtained by Baker and by Dixon for most cases of combination.

J. W.

**Polymeric Thiocarbonyl Chloride.** By G. CARRARA (*Gazzetta*, 23, ii, 12—17).—By means of cryoscopic determinations in benzene solution, the author confirms the generally accepted view that the polymeride of thiocarbonyl chloride has the molecular composition  $(\text{CSCl}_2)_n$ ; the thermometric depressions indicate a small but increasing amount of dissociation as the solutions become more dilute. The refraction constants of thiocarbonyl chloride, of its polymeride and of perchloromethylmercaptan were also determined for the  $\alpha$ ,  $\beta$ , and  $\gamma$  hydrogen lines and the D line; the principal results are given in the following table.

Substance.	$t$ .	$\frac{P^{\mu_{H_a}} - 1}{d}$ .	$P \frac{\mu_{H_a}^2 - 1}{(\mu_{H_a}^2 + 2)d}$ .	Atomic refraction of sulphur.	
				From $\mu$ .	From $\mu^2$ .
$\text{S}:\text{CCl}_2$ .....	$9.0^\circ$	40.20	23.37	15.60	8.85
$\text{S}:\text{CCl} \cdot \text{S} \cdot \text{CCl}_2$ ..	$\begin{cases} 12.4 \\ 11.9 \end{cases}$	$\begin{cases} 76.54 \\ 76.70 \end{cases}$	$\begin{cases} 43.94 \\ 43.94 \end{cases}$	13.71	7.45
$\text{SCl} \cdot \text{CCl}_2$ .....	11.0	58.93	34.19	14.73	7.63

The measurements for the polymeric thiocarbonyl chloride were made on benzene solutions containing 16.139 and 15.549 per cent. respectively. It is noteworthy that the atomic refractions of sulphur

deduced from these observations are considerably smaller than those observed by Nasini and Costa with similar compounds.

W. J. P.

**Magnesium Nitride.** By A. SMITS (*Rec. Trav. Chim.*, 12, 198—202).—Magnesium nitride is prepared by heating magnesium powder in a current of dry ammonia. It is a yellow substance, easily powdered, and must be kept in sealed tubes, as it is rapidly acted on by the moisture of the air. Although immediately decomposed by water, it is not acted on by glycerol or by oxalic acid dissolved in absolute alcohol. Nitrate of silver in alcoholic solution is reduced.

A quantitative synthesis establishes the composition  $Mg_3N_2$ , a result confirmed by analyses.

W. T.

**Lead Tetrachloride.** By H. FRIEDRICH (*Monatsh.*, 14, 505—520; compare *Abstr.*, 1890, 699; 1893, ii, 415; also Classen and Zahorski, *ibid.*, 1893, ii, 464).—The author confirms the formula  $PbCl_4 \cdot 2NH_4Cl$  for the double chloride of lead and ammonium, to which Classen and Zahorski (*loc. cit.*) gave the formula  $2PbCl_4 \cdot 5NH_4Cl$ , and is of the opinion that the compound analysed by those investigators contained free ammonium chloride. The behaviour of the double salt on adding it to well-cooled sulphuric acid, whereby lead tetrachloride separated as an oily substance, was so remarkable that the author investigated the behaviour of ammonium stannichloride towards sulphuric acid, and obtained a similar result, tin tetrachloride being formed. The tetrachlorides of lead and tin therefore closely resemble each other in regard to their stability in presence of sulphuric acid, and tin and germanium tetrachlorides may even be distilled from the concentrated acid without decomposition. On the other hand, the higher chlorides of iron and of antimony are readily decomposed by the acid with evolution of hydrogen chloride. Attempts to isolate lead tetrabromide or its double salt with an alkaline bromide have proved unsuccessful.

G. T. M.

**Basic Copper Selenate and Basic Cobalt Selenate.** By BOGDAN (*Bull. Soc. Chim.*, [3], 9, 584—586).—Basic copper selenate,  $2SeO_3 \cdot 3CuO \cdot 4H_2O$ , or  $Cu(O \cdot SeO_3 \cdot OCo \cdot OH)_2 \cdot 3H_2O$ , is obtained by heating a 10 per cent. solution of normal copper selenate in sealed tubes at  $240$ — $250^\circ$  for several hours. It forms minute, transparent, emerald-green, prismatic crystals, insoluble in water but easily soluble in acids. When heated at about  $250^\circ$ , the salt loses water and decomposes with liberation of selenium. The fact that the salt does not lose water at  $210^\circ$  is not regarded by the author as evidence that the water is not present in the form of water of hydration.

Basic cobalt selenate,  $3SeO_3 \cdot 4CoO \cdot H_2O$ , or



is obtained in a similar manner, and forms small, red, acicular crystals strictly analogous to the copper compound in general properties.

C. H. B.

Hydrogen com- pounds.	Lithium com- pounds.	Ammonium compounds.		Sodium com- pounds.	Potassium com- pounds.
—	$\text{MnCl}_3, \text{LiCl}, 3\text{H}_2\text{O}$	$\text{MnCl}_3, \text{NH}_4\text{Cl}, 2\text{H}_2\text{O}$	$\text{MnCl}_3, 2\text{NH}_4\text{Cl}, 11\text{H}_2\text{O}$	—	—
—	$\text{FeCl}_3, \text{LiCl}, 3\text{H}_2\text{O}$	—	$\text{FeCl}_3, 2\text{NH}_4\text{Cl}$	—	$\text{FeCl}_3, 2\text{KCl}$
—	$\text{NiCl}_3, \text{LiCl}, 3\text{H}_2\text{O}$	$\text{NiCl}_3, \text{NH}_4\text{Cl}, 6\text{H}_2\text{O}$	—	—	—
$\text{CoCl}_3, \text{HCl}, 3\text{H}_2\text{O}$	$\text{CoCl}_3, \text{LiCl}, 3\text{H}_2\text{O}$	$\text{CoCl}_3, \text{NH}_4\text{Cl}, 6\text{H}_2\text{O}$	—	—	—
$\text{CuCl}_3, \text{HCl}, 3\text{H}_2\text{O}$	$\text{CuCl}_3, \text{LiCl}, 2\frac{1}{2}\text{H}_2\text{O}$	$\text{CuCl}_3, \text{NH}_4\text{Cl}$	$\text{CuCl}_3, 2\text{NH}_4\text{Cl}, 2\frac{1}{2}\text{H}_2\text{O}$	—	$\left\{ \begin{array}{l} \text{CuCl}_3, 2\text{KCl}, 2\text{H}_2\text{O}, \\ \text{CuCl}_3, \text{KCl} \end{array} \right.$
$\text{CdCl}_3, \text{HCl}, 3\frac{1}{2}\text{H}_2\text{O}$	$\text{CdCl}_3, \text{LiCl}, 3\frac{1}{2}\text{H}_2\text{O}$	$\text{CdCl}_3, \text{NH}_4\text{Cl}, \frac{1}{2}\text{H}_2\text{O}$	—	—	$\text{CdCl}_3, \text{KCl}, \frac{1}{2}\text{H}_2\text{O}$
$\text{SnCl}_3, \text{HCl}, 3\text{H}_2\text{O}$	$\text{SnCl}_3, \text{LiCl}, 4\text{H}_2\text{O}$	—	$\text{SnCl}_3, 2\text{NH}_4\text{Cl}$	$\text{SnCl}_3, 2\text{NaCl}, 5\text{H}_2\text{O}$	$\text{SnCl}_3, 2\text{KCl}$

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**New Double Chlorides.** By A. CHASSEYANT (*Ann. Chim. Phys.*, [6], 30, 5—56; compare Abstr., 1892, 118 and 1275).—The author has prepared and analysed most of the double salts the formulæ of which appear in the table (preceding page); some of these are new, whilst others have already been described by himself and others. The arrangement renders clear the relations and differences which exist between the salts. A. R. L.

**Decomposition of Alkali Stannates under the influence of Carbonic Anhydride and of Alkali Carbonates.** By A. DITTE (*Ann. Chim. Phys.*, [6], 30, 282—285).—Austen has shown (*Chem. News*, 46, 286) that stannic oxide may be readily prepared by passing a current of carbonic anhydride into a solution of an alkali stannate containing an excess of alkali.

When some bubbles of carbonic anhydride are allowed to fall on the surface of a dilute solution of an alkali stannate, a cloudy separation of gelatinous stannic oxide rises to the surface, and, as it increases in amount, the carbonic anhydride ceases to be absorbed. When, however, the carbonic anhydride is introduced very slowly in contact with crystals of stannate, a dense monhydrated stannic oxide is formed, which seems to be amorphous. If carbonic anhydride is passed into a mixture of stannate and carbonate, stannic oxide falls to the bottom of the liquid. Alkali carbonate free from the acid salt does not give rise to the production of stannic oxide when added to a stannate; stannic oxide is formed in amount proportional to the quantity of acid salt present. A. R. L.

**Preparation of Potassium Metantimonate.** By DUK (*Chem. Centr.*, 1893, ii, 254; from *Bull. Soc. roy. Pharm. Bruxelles*, 37, 109).—The method depends on eliminating the sulphur from the sulphantimonate by means of copper oxide. Black antimony sulphide (100 grams), potassium carbonate (150 grams), slaked lime (100 grams), and sulphur (20 grams) are shaken with 12 litres of water, and after remaining eight days the mixture is filtered. The filtrate, which contains potassium sulphantimonate, is boiled with copper oxide (120 grams) and filtered. The filtrate is diluted with water and treated with carbonic anhydride, when potassium metantimonate is precipitated. E. C. R.

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## Mineralogical Chemistry.

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**Canfieldite, a new Germanium Mineral.** By S. L. PENFIELD (*Amer. J. Sci.*, 46, 107—113).—This new mineral was brought from Bolivia by F. A. Canfield. It crystallises in combinations of the octahedron and rhombic dodecahedron. The fracture is conchoidal, the hardness 2.5, the sp. gr. 6.27, the colour black, the streak greyish-black, and the melting point very low. The mineral consists of

silver, germanium, and sulphur, and has the same quantitative composition as argyrodite. Analysis gave the following results:—

S.	Ge.	Ag.	Total.
17.10	6.57	76.33	100.00

Thus canfieldite and argyrodite have the same chemical composition, which is  $\text{Ag}_5\text{GeS}_8$ .

A new analysis, made by the author, of argyrodite from Freiberg gave

S.	Ge.	Ag.	Total.
16.83	6.69	76.48	100.00

The mineral  $\text{Ag}_5\text{GeS}_8$  is therefore dimorphous, canfieldite being isometric and argyrodite monoclinic. B. H. B.

**Natural Manganese Oxides: Polianite and Pyrolusite.** By A. GORGEU (*Bull. Soc. Chim.*, [3], 9, 496—502).—The author has examined a specimen of polianite from Platten, in Bohemia, and specimens of crystallised pyrolusite from many localities in Central and Eastern Europe. The hardness of the polianite was 6.5, and its sp. gr. 5.03 to 5.09; whilst the hardness of the pyrolusite varied from 2.5 to 5.0, and the sp. gr. from 4.75 to 5.10, according to the degree of hydration. Only the polianite was really anhydrous, and the proportion of water in the pyrolusite varied from 0.75 to 2.65 per cent., only about one-third being given off in a vacuum, and a further quantity at about 280°. The temperature of decomposition of the pyrolusites is above 460°, and is identical with that of the artificial varieties. When incompletely dissolved by hydrochloric acid, the residue has the composition of manganese peroxide. Boiling nitric acid, concentrated or dilute, dissolves only a trace of manganese.

The impurities in the pyrolusites are practically the same in all cases, namely, iron, calcium, magnesium, lead, barium, potassium, and sodium, and sulphuric, carbonic, phosphoric, and arsenic acids; they are present only in small proportion. The percentage of manganese anhydride,  $\text{MnO}_2$ , present after abstraction of the impurities varies from 98 to 100 per cent. C. H. B.

**Rowlandite.** By W. E. HIDDEN and W. F. HILLEBRAND (*Amer. J. Sci.*, 46, 208—212).—About 2 lbs. of this mineral was found by W. E. Hidden, in a shipment of yttria-bearing minerals from Llano Co., Texas. The mineral is isotropic; its hardness is 6; its sp. gr. 4.513 at 15.5°; its fracture glassy-conchoidal; its lustre vitreous-resinous; and its streak is greenish-grey. An analysis by W. F. Hillebrand gave the following results:—

$\text{SiO}_2$ .	$\text{Ce}_2\text{O}_3$ .	La group.	Y group.	$\text{FeO}$ .	$\text{MnO}$ .	$\text{MgO}$ .	F.
26.04	5.06	9.34	47.70	4.39	0.67	1.62	3.87

These are in accord with the empirical formula  $\text{Si}_4\text{R}_4\text{F}_2\text{O}_{14}$ .

B. H. B.



**Zoisite from North Carolina.** By W. E. HIDDEN (*Amer. J. Sci.*, 46, 154).—Very pure monazite at the Flat Rock mine, Mitchell Co., North Carolina, was found by the author to be surrounded by a pink, vitreous zoisite associated with a black, glassy allanite. An analysis of the zoisite gave the following results:—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	MnO.	CaO.	H <sub>2</sub> O.	Total.
39.98	31.02	4.15	0.23	23.80	2.03	100.21

The sp. gr. is 3.352 at 27°.

B. H. B.

**Mackintoshite, a new Thorium and Uranium Mineral.** By W. E. HIDDEN and W. F. HILLEBRAND (*Amer. J. Sci.*, 46, 98—103).—With thorogummite and cyrtolite in Llano Co., Texas, a new mineral has been discovered. It is opaque and black, but not quite so dull in lustre as the associated cyrtolite. A strong lens is necessary to distinguish the two. The hardness of the mineral is 5.5, and no trace of cleavage has been observed. The fracture is sub-conchoidal to hackly, and the sp. gr. is 5.438 at 21°. Its form is tetragonal, and resembles zircon and thorite in habit and angle. Square prisms, sometimes 1 cm. thick, with a simple pyramid, are all the forms thus far observed. It also occurs massive, nodular, and filling veins in cyrtolite and fergusonite embedded in coarse pegmatite. It is infusible before the blowpipe, and is not entirely decomposed by any one acid. Analysis gave results in accord with the formula  $UTh_3Si_3H_8O_{18}$ , the formula of thorogummite being  $UTh_3Si_3H_{12}O_{21}$ .

B. H. B.

**Alnoite containing Melilite.** By C. H. SMYTH (*Amer. J. Sci.*, 46, 104—107).—The author described (Abstr., 1892, 1057) a small dyke occurring in a fault fissure at Manheim, New York. Recently some sections have been prepared from fresher material, and these show that one of the constituents is melilite, a supposition that the author originally hesitated to accept. Upon the basis of its mineralogical composition, and from a comparison with a specimen from Alnö, the rock must be classed as alnoite. The optical properties of the melilite are fully described, the mineral, although consisting chiefly of positive material, having patches of a negative character scattered through them.

B. H. B.

**Actinolite Magnetite Schists in Minnesota.** By W. S. BAYLEY (*Amer. J. Sci.*, 46, 176—180).—Attention has repeatedly been called to the existence of beds of amphibole schists associated with the ores in the older iron ore regions of the Lake Superior district. Consequently, their discovery on the newly opened Mesabi range is of interest from a theoretical standpoint. The descriptions of them given by the author agree very closely with those given by Irving and Van Hise (Abstr., 1892, 794) for the corresponding schists in the Penokee series, except that in the Minnesota rocks quartz is rare, and hæmatite is absent. The presence of these peculiar rocks in the Mesabi range is noteworthy, since their origin in other districts has

been thought to be closely connected with that of the iron ores with which they are associated. B. H. B.

## Physiological Chemistry.

**Oxidation of Methylic and Ethylic Alcohols in the Organism.** By J. POHL (*Chem. Centr.*, 1893, ii, 380—381; from *Arch. Expt. Path. Pharm.*, 31, 281—302).—Ethylic alcohol administered to a dog produces protracted sleep, and when this passes off, the dog awakes in a normal condition. Methylic alcohol, on the other hand, produces restlessness, giddiness, and then broken sleep; and the effects of a dose last for three or four days. A dog may be dosed without harm for a year with ethylic, isobutylic, or amylic alcohol; but with methylic alcohol death ensues in a few weeks.

In the case of poisoning by methylic alcohol, formic acid appears in the urine, and reaches a maximum on the third or fourth day.

E. C. R.

**Presence of Ammonia in the Stomach, and its Influence on the Estimation of the Hydrochloric acid.** By H. STRAUSS (*Chem. Centr.*, 1893, ii, 379—380; from *Berlin. Klin. Woch.*, 30, 398—402).—The author confirms Rosenheim's results (*Abstr.*, 1893, ii, 177).

The only method of estimating the chlorine which is not influenced by the presence of ammonium chloride is Leo's method; the free and combined hydrochloric acid is converted into calcium chloride by means of calcium carbonate, which does not decompose the acid phosphates, and the acidity is determined before and after this treatment.

E. C. R.

**Mineral Matter of Bones and Teeth.** By S. GABRIEL (*Zeit. physiol. Chem.*, 18, 257—303).—The mineral matters in bone and teeth contain lime, magnesia, potash, soda, water, phosphoric acid, carbonic anhydride, chlorine, and fluorine; there is, in addition, a substance which, when fused, turns red. The quantities of lime and phosphoric acid, which are the most abundant constituents, vary but little, and are proportional one to the other; the amounts of magnesia and carbonic anhydride are also proportional to each other. The amount of potash is greater than that of soda. The quantity of chlorine is very small, and is greater in the teeth (0.21 per cent.) than in bone. Fluorine is the minimal constituent of both (as a rule not over 0.05 per cent.), and is not more abundant in teeth than in bone.

Water is present in two forms: one part, passing off at 300—350°, is similar to water of crystallisation; the other part is only expelled by fusion with silicic acid, and is an expression of the basicity of the phosphate, and is called water of constitution or acidic water.

The bone phosphate has a basic character, containing 15 equivalents of acid to 16 of base; and it is probably a loose union of a

normal with a basic phosphate. The composition of the ash finds its simplest expression in the formula  $\text{Ca}_3(\text{PO}_4)_2 + \text{Ca}_5\text{HP}_3\text{O}_{13} + \text{Aq}$ , in which 2 to 3 per cent. of the lime is replaced by magnesia, potash, and soda, and 4 to 6 per cent. of the phosphoric acid by carbonic anhydride, chlorine, and fluorine. The limit of variation is, however, small; and the differences between bone ash and tooth ash are not greater than those between the ash of different bones.

W. D. H.

**Amount of Fluorine in Teeth.** By E. WRAMPMEYER (*Zeit. anal. Chem.*, 32, 550—553).—The author employed Carnot's method (Abstr., 1892, 911), and obtained the following numbers.

Healthy teeth of adults.....	1.37 per cent. of fluorine
Diseased     "     "     .....	1.16     "     "
Healthy     "     children.....	0.65     "     "
Diseased     "     "     .....	1.40     "     "

whence he infers that no direct conclusion as to the soundness of teeth can be drawn from the percentage of fluorine they contain.

Each sample of teeth consisted of 4 molars, 2 incisors, and 1 canine tooth. Test analyses with pure potassium silicofluoride gave 93.5 and 93.8 per cent.

M. J. S.

**Chemistry of the Refractive Media of the Eye.** By C. T. MÖRNER (*Zeit. physiol. Chem.*, 18, 213—256; compare Abstr., 1893, ii, 424).—*The Cornea.*—This is considered in its separate layers. The *substantia propria* of the cornea was considered by Müller to consist of a chondrogenous substance similar to that found in hyaline cartilage. Morochowetz showed that chondrin, here as elsewhere, is not a chemical unit, but a mixture of gelatin with a mucinoid material. This has been confirmed since then, and special attention is here paid to the mucinoid material, which is here called *cornea-mucoid*. It was extracted with dilute alkali, and precipitated from the extract by acetic or hydrochloric acid. Its percentage composition is C, 50.16; H, 6.97; N, 12.79; S, 2.07; O, 28.01. It closely resembles in its properties the mucoïds found in hyaline cartilage and the vitreous humor, and the pseudo-mucin of ovarian fluid. The gelatin obtained from the collagen, the other main constituent of the cornea, resembles that obtained from other sources. The mucoïd and collagen of the sclerotic are identical with those obtained from the cornea.

Only traces of pure proteïd matter are obtainable from the *substantia propria* of the cornea; the larger quantities previously described originated doubtless from the epithelial layer. This layer yields abundance of proteïd matter which very closely resembles paraglobulin in its properties. Nucleïn was not obtained, neither was any trace of myosin found. Descemet's membrane resembles in its chemical properties the membranes of the lens and vitreous humor. These membranes consist of a mechanical mixture of a mucinoid material with sparingly soluble, nitrogen-rich (14.77 per cent.) albuminoid substance, which agrees in its properties neither with collagen nor

with elastin. Descemet's membrane is not digested by either gastric or pancreatic juice, but the lens capsule is completely dissolved. The solubilities of the lens capsule in other reagents are greater than those of Descemet's membrane. The main substance of the lens capsule is very like elastin.

*The Vitreous Humor.*—The fluid filtered off from the vitreous humor contains proteid and mucin. Observers differ as to the variety of proteid present, and also as to the presence or absence of mucin. It was found necessary to dilute the fluid very considerably before acetic acid caused a precipitate of mucin. This may account for the discrepancy. It is regarded as a mucoïd rather than as mucin proper; it contains 12.27 nitrogen and 1.19 sulphur per cent. The membranes of the vitreous yield gelatin.

*Aqueous Humor.*—This contains proteid, but no mucin.

W. D. H.

**Absence of Bile Acids, Hippuric acid, and Benzoic acid from the Suprarenal Capsules.** By H. STADELMANN (*Zeit. physiol. Chem.*, 18, 380—396).—Recent experiments on the functions of the suprarenal capsules render it necessary that exact knowledge should be obtained of their chemical composition. The present research shows that certain substances described by other authors in the glands, namely, bile acids, hippuric and benzoic acids, are not present.

W. D. H.

**Proteids of Milk.** By M. ARTHUS (*Arch. de physiol.*, 1893, 673—677).—The experiments show that, in addition to caseinogen, milk contains other proteids. These differ from caseinogen in being coagulable by heat, and, like Sebelien, the author separates them into lactalbumin and lactoglobulin.

W. D. H.

**Alcaptonuria.** By H. EMBDEN (*Zeit. physiol. Chem.*, 18, 304—334; compare Abstr., 1893, ii, 82).—It has been abundantly shown since the publication of Wolkow and Baumann's researches on this subject (Abstr., 1891, 1128; 1892, 925), that the abnormal substance known as alcapton is homogentisic acid. References to published cases are given; in one of these glycosuria was present as well. The present paper relates to certain experiments on metabolism, performed with a view of testing the correctness of the hypothesis that the abnormal constituent of the urine originates by an unusual form of metabolism from tyrosine.

The first experiments were performed on the patient alluded to in the author's previous publication. It was found that the acid in the urine was increased by a flesh diet, that the administration of tyrosine doubled the excretion of the acid, that phenylacetic and phenylamido-acetic acids had no such influence, that oil of turpentine, kephir, and castor oil, although lessening the combined sulphates of the urine due to lessened putrefaction in the alimentary canal, had little or no influence on the amount of homogentisic acid. On administering the acid by the mouth, about 75 per cent. was excreted in the urine. Another point noted in the urine of this patient was an abnormally low excretion of uric acid (estimated by Fokker's method). The second series of experiments performed on healthy men and animals

showed that after the administration of the acid (by the mouth in man and by subcutaneous injection in dogs), the urine assumed all the characters of the urine of alcaptonuria, the amount of acid recovered in the urine being considerable, but nevertheless indicating that some had been destroyed in the living tissues. W. D. H.

**Rare Urinary Calculi.** By J. HORBACZEWSKI (*Zeit. physiol. Chem.*, 18, 335—340).—The first stone examined was a fatty concretion, and analysis gave the following result.

	Per cent.
Water .....	2.5
Ash .....	0.8
Organic matter insoluble in ether .....	11.7
Organic matter soluble in ether .....	85.0
Containing—	
Free fatty acids .....	51.5
Fats .....	33.5
Cholesterol.....	traces.

The organic matter insoluble in ether contained insoluble soaps of calcium and magnesium, and probably some blood proteid and mucin.

The second stone was a cholesterol concretion. It contained—

	Per cent
Water.....	8.76
Ash .....	0.55
Organic matter .....	95.99
Containing—	
Cholesterol.....	95.87
Organic matter insoluble in ether ....	0.15

W. D. H.

## Chemistry of Vegetable Physiology and Agriculture.

**Cellulose in Bacilli and other Fungi.** By I. DREYFUS (*Zeit. physiol. Chem.*, 18, 358—379).—The organisms investigated were *Polyporus*, *Agaricus campestris*, *Bacillus subtilis*, pus bacilli, and *Aspergillus glaucus*. It was found that all contain "true cellulose," in E. Schulze's sense. The presence of hemi-cellulose is very doubtful.

Cellulose was also found in caseating lymph glands, and thus an observation of Freund's is confirmed. It doubtless is due to the bacilli in the tuberculous deposits. W. D. H.

**Decomposition of Hydrogen Peroxide by Cells.** By A. GORTSTEIN (*Virchow's Archiv*, 133, 295—307).—Liebreich was the first to

use hydrogen peroxide for distinguishing between living bacteria and those killed by heat, the former decomposing the peroxide, the latter not. This evolution of oxygen is here recommended as a macroscopic test for the presence of bacteria, for instance, in drinking water.

Many living cells act in the same way, so also do certain proteïds, such as fibrin, which are non-living.

The present experiments show that this power of the cells does not necessarily depend on the life of the cells; many vigorous antiseptics do not prevent it; certain substances, however, which are not antiseptics in the narrow sense do destroy the power; those particularly mentioned being hydrocyanic acid, chloral hydrate, and chloral cyanhydrin. Heating to 70° destroys the power, unless the cells are dried, when it has not this effect.

It is further shown that nucleïn prepared from yeast, pus, liver, and other cells possesses the power of decomposing hydrogen peroxide. Negative results were, however, obtained with nucleic acid and artificial nucleïn, but the number of experiments in which these were used was small. The theory is advanced that cells, bacteria, and proteïds act in this way in virtue of the nucleïn they contain, and the process is regarded as a chemical rather than a catalytic phenomenon.

W. D. H.

**Cause of Electric Currents observed in Plants.** By O. HAACKEL (*Ann. Agron.*, 19, 396—399; from *Bot. Centr.*, 54, 13).—According to Künckel, electric currents in plants are due to the movements of water in the tissues, and not to differences of potential, existing independently. The author considered it probable that vegetable electricity was due to biological processes, especially respiration and the consequent chemical changes. He experimented with leaves and flowers of dicotyledons and on a large mushroom in an atmosphere of hydrogen. The electric current was diminished, but never quite suppressed, owing, probably, to intramolecular respiration. On readmitting air, the electric current revives. Young bean plants behaved differently, the current being increased in an atmosphere of hydrogen. This is explained by the known fact that beans are distinguished by a very high intramolecular respiration.

Flowers, and especially stamens and pistils, show very decided oscillations under the influence of electric currents.

It is not possible to state exactly in what manner respiration gives rise to electric currents without a knowledge of the successive chemical changes which take place during respiration. The results of the author's experiments seem to indicate that vegetable electricity is not exclusively due to filtration of water.

N. H. M.

**Influence of Carbonic Oxide on Germination.** By A. MARCACCIO (*Uhem. Centr.*, 1893, ii, 376; from *Arch. ital. Biol.*, 19, 140).—Carbonic oxide, in a similar manner to chloroform and ether, prevents the germination of seeds, and retards the process of putrefaction and the growth of micro-organisms.

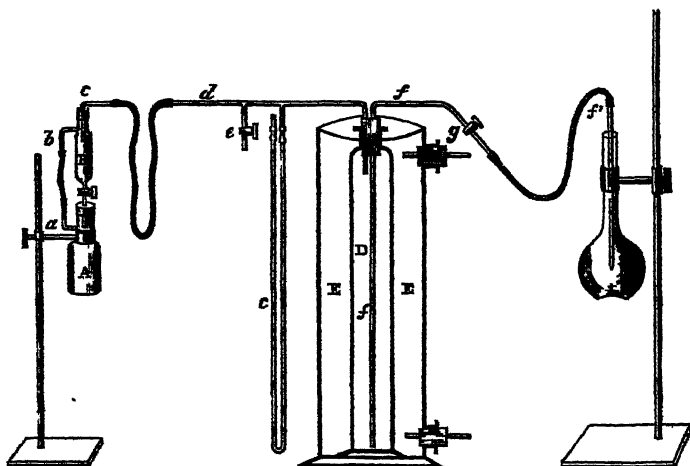
E. C. R.

**Mannitol and Dulcitol in the Vegetable Kingdom.** By A. N. MONTEVERDE (*Ann. Agron.*, 19, 444—446; from *Bct. Centr.*, Bei-

hefte 3, 199).—Mannitol and dulcitol are true plastic substances in the case of *Rhinanthus*, *Euphrasia*, and *Melampyrum*; they disappear when the plants are kept in the dark, and reappear under more favourable biological conditions; but they nourish only such plants as contain them normally. When *Rhinanthus* and *Euphrasia* are fed with glucose or cane sugar, mannitol is produced; *Melampyrum* similarly fed yields dulcitol. *Scrophularia nodosa*, contrary to what has been stated, contains neither one nor the other, and has not the power of transforming them into starch. *Euonymus europæus* contains much dulcitol at the budding period, but none in winter. The same holds (for mannitol) in the case of *Syringa vulgaris*. An examination of 797 species of *Scrophulariaceæ* showed that mannitol is present in 272 species, dulcitol in 26 species. It thus seems that the presence of one or the other of these carbohydrates is a constant character not only of an order, but also of a sub-order. Mannitol occurs in some *Orobanchaceæ*, in the *Oleaceæ* (A. Mayer) in celery and parsley. Some *Celastraceæ* contain dulcitol. N. H. M.

### Analytical Chemistry.

**New Gas-volumeter of General Applicability.** By F. GANTTER (*Zeit. anal. Chem.*, 32, 553—564).—The principle of the method consists in the measurement of a liquid expelled by the evolved gas.



The cylinder D and tube *f* are filled to the point of *f'* with a liquid in which the gas to be liberated is not soluble: *g* is then closed. For carbonic anhydride, a solution of calcium chloride of sp. gr. 1.4 serves

well. The substance is weighed into A, and the reagent placed in B, and A and B are then plunged into the water-jacket E. When equilibrium of temperature is attained, pressure is equalised by opening *e* for a moment. The tube *f'* is now placed in an empty flask of known capacity, and *g* is opened. The gas is next evolved by allowing the reagent to flow into A, and the contents of A are boiled, the internal pressure being all the time maintained below that of the atmosphere by keeping the point of *f'* at a lower level than the surface of the liquid in D, but as soon as cooling commences *f'* must be raised so as to produce a small excess of internal pressure, and its point must be kept plunged in the liquid in the flask. The reaction vessels are again plunged into the water in E, and when cooling is complete *f'* is lowered until the manometer C shows that the pressure is the same as at the outset; *g* is then closed, *f'* removed from the flask, and the unoccupied portion of the flask measured by filling up to the mark from a burette. It is necessary that the temperature of E should be exactly the same at the end as at the beginning, and if it is desired to avoid reduction of the gas volume to normal temperature and pressure, an experiment with a pure substance will give in half an hour a factor for direct calculation from the observed volume under the existing conditions.

In estimating ammonia by decomposition with hypobromite, it is best to put the hypobromite in A, and the ammoniacal solution in B, and, finally, to rinse B thrice with the hypobromite by inclining the apparatus so that the liquid flows from A through *a* and *b* to B.

Nitric acid can also be estimated by decomposition with copper and sulphuric acid, but for this purpose a special laboratory vessel is required, from which the air can be expelled by hydrogen.

M. J. S.

**Borax as a Basis for Acidimetry.** By T. SALZER (*Zeit. anal. Chem.*, 32, 529—537; see Rimbach, *Abstr.*, 1893, ii, 232).—The author suggested the use of borax as a standard alkali in 1857, but the impossibility of obtaining solutions of normal strength operated against its adoption at the time. It is, however, far preferable to work with weak solutions, since the tendency of boric acid to redden litmus disappears on dilution. Methyl-orange may be used as indicator in the titration of mineral acids, but in dilute solutions is far less sensitive than litmus: for organic acids it is inadmissible. The borax used must be free from octahedral crystals; it should lose 47.1 per cent. of water when ignited. A decinormal solution (19.0872 grams per litre) is of convenient strength, and acids must be diluted to a strength not exceeding N/10 before titration. The acid is to be coloured a pale yellowish-red with sensitive litmus tincture, and the borax solution run into it until the colour just changes to a bluish-red, and no longer returns to yellowish-red on stirring. Mineral acids, oxalic, acetic, and tartaric acids give satisfactory results; phosphoric acid behaves like a monobasic acid. These acids give practically the same results when the acid is run into the borax as when the process is reversed. Citric acid can equally well be titrated by the borax solution, but when the citric acid is run into the borax more acid is consumed, seemingly from formation of borocitric acid. M. J. S.



**Phenolphthaleïn as an Indicator.** By R. T. THOMSON (*J. Soc. Chem. Ind.*, 12, 432—433).—The author has found that boric acid may be accurately titrated with standard solution of sodium hydroxide, using phenolphthaleïn as indicator, but it is necessary to add to the liquid about one-third of its bulk of glycerol. The amount of boric acid contained in borax may be estimated in the same manner, after first adding sufficient sulphuric acid to combine with the soda, methyl-orange serving as indicator. The excellent results obtained by the author are probably due to the greater viscosity of the liquid, caused by introducing the glycerol. L. DE K.

**Extraction of the Gases Dissolved in Water.** By J. ROBSON (*J. Soc. Chem. Ind.*, 11, 504).—The apparatus used is a modification of that of Kreusler for the estimation of nitric acid. The gases are boiled out from the water in a flask from which the air has been completely expelled by steam, and are collected in a vertical cylinder of 150 c.c. capacity, closed at its lower end by a cork, and at its upper end connected by a rubber tube to a Schiff's nitrogen measurer. Through the cork of this cylinder pass two tubes, the one connected to the long narrow neck of the extraction flask, and the other with a reservoir of boiling distilled water at a higher level. A figure shows the arrangement of the apparatus and the mode of using it.

M. J. S.

**Estimation of Dissolved Oxygen.** By G. ROMJN (*Rec. Trav. Chim.*, 12, 241—247).—The sample of water is taken from any required depth beneath the surface by means of a pipette of known volume. The pipette is furnished with three-way stopcocks above and below, the upper stopcock having above it a small bulb with a fiducial mark on its free neck, and of known volume, about one-twentieth the capacity of the pipette. The pipette is filled by the aid of a small pump, the liberation of dissolved gases from the water in the pipette, owing to reduction of pressure due to the action of the pump, is avoided by having the aperture of the lower stopcock of double the diameter of that next the bulb. The upper three-way tap allows of the water sampled being drawn through the pipette in quantity sufficient to ensure the purity of the sample.

The pipette being full and the upper bulb empty, the lower tube is connected with a reservoir containing sodium hyposulphite ( $\text{Na}_2\text{SO}_3$ ) solution, and a little of the solution is run through the stopcock to wash out the tube and tap; the bulb is then placed in communication with the pipette, and, the lower cock being turned, hyposulphite solution is run in until the displaced water reaches the mark on the neck of the bulb; the taps are now turned off at both ends of the pipette, and the whole set aside for about ten minutes. The same volume of iodine solution is then introduced in the same manner, the lower tap and tube washed with water, the remaining contents of the pipette transferred to a flask, and the residual iodine determined by thiosulphate in the usual way.

The hyposulphite solution is kept in a bottle connected with a small hydrogen generator, arranged so as to keep an atmosphere of

hydrogen under pressure over the solution, the pressure being sufficient to force the solution into the pipette.

If  $V$  be the volume of the pipette,  $v$  the volume of the bulb between the mark and the upper tap, then the volume of water ultimately used for the titration is  $(V - v)^2/V$ .

Let  $O$  be the titre of oxygen, in cubic centimetres per litre of water, then  $O = (A - B)a$ . In this formula,  $A$  represents the number of cubic centimetres of thiosulphate used,  $B$  the number of cubic centimetres of thiosulphate which would be used for water free from oxygen, and  $a$  is a constant depending on the dimensions of the pipette and the titre of the thiosulphate solution.

$B$  can best be determined by an experiment with water saturated with air at a known temperature, of which the oxygen titre is known from Roscoe and Lunt's or Winkler's determinations. The constant

$$u = \frac{8000}{1.43} \cdot \frac{V}{(V - v)^2} \cdot r$$
 In this formula,  $\frac{1000 V}{(V - v)^2}$  is the factor for calculating from the volume of water used, the figure for a litre of water;  $8/1.43$  is the factor reducing the weight-equivalent of oxygen to the corresponding volume equivalent; and  $r$  is the factor used in reducing the actual volume of thiosulphate used to the equivalent volume of normal solution.

A correction is required if the water contains any substance such as hydrogen sulphide, which itself absorbs iodine, or when only about 2 c.c. of oxygen per litre is found and the deficiency is caused by a rapid decomposition of organic matter; this is found by a preliminary experiment to determine the iodine so absorbed. W. T.

**Detection of Iodic acid in Nitric acid.** By E. PIESZCZEK (*Chem. Centr.*, 1893, ii, 337; from *Apoth. Zeit.*, 8, 322).—The iodic acid is reduced with hydrogen sulphide, tin filings, or sulphurous anhydride. It is most convenient to use tin, in which case 10 c.c. of the acid is gently warmed with a few scraps of tin, and, after a few minutes, shaken with a small quantity of chloroform, which remains colourless in the absence of iodine or iodic acid. E. C. R.

**Influence of Ammonia on the Estimation of Hydrochloric acid in the Stomach Contents.** By H. STRAUSS (*Chem. Centr.*, 1893, ii, 379—380; from *Berlin Klin. Woch.*, 30, 398—402).—See this vol., ii, 21.

**Estimation of Phosphorus in Steel and Iron containing Silicon.** By J. SPÜLLER and S. KALMAN (*Zeit. anal. Chem.*, 32, 538—550).—In the precipitation of phosphoric acid by molybdate from solutions containing silica, a certain quantity of a silicomolybdate is apt to separate. This precipitation is much favoured by the presence of ammonium salts, especially the nitrate; potassium nitrate is without influence. The lower the temperature at which the precipitation takes place, the smaller the amount of silicomolybdate formed, so that by proceeding in the following manner a correct determination can be made even in presence of silica. Of steel, 3.3 grams is dissolved in 50—55 c.c. of nitric acid (1.2 sp. gr.) in a  $\frac{1}{4}$  litre conical

flask, at first in the cold, but finally with vigorous boiling. When all nitrous vapours are expelled, the solution is treated with 8 c.c. of a 3 per cent. solution of potassium permanganate, and boiled until the red colour disappears. The precipitated manganic oxide is reduced by adding 4 c.c. of a 10 per cent. solution of potassium nitrite, and, after cooling to 55—60°, the phosphoric acid is precipitated by adding 80 c.c. of molybdate, or, equally well, it may be cooled completely before adding the molybdate, and then warmed to 40°. The mixture is now kept for two hours at 36—40°, with an occasional shake; the precipitate which forms is collected, and since it has a tendency to pass through the filter, this should be prepared by pouring upon it a thin pulp of paper fibres. The molybdate solution is made by dissolving 150 grams of ammonium molybdate to a litre, and pouring it into a litre of nitric acid (1.2 sp. gr.). The precipitates, after being washed, first with a mixture of 100 vols. of molybdate solution, 20 vols. of nitric acid, and 80 vols. of water, and then with a 10 per cent. solution of ammonium nitrate, are dissolved from the filter with a little dilute ammonia, and the solution evaporated and gently ignited in small porcelain basins until the ammonium salts are expelled.

Cast iron requires 60—80 c.c. of nitric acid to dissolve 3.3 grams, and should be very finely powdered. It usually contains so much phosphorus that only one-half to one-fifth of the solution need be precipitated, and if so much silica is present that part of it separates as a gelatinous precipitate, the solution should be made up to a known volume, and run through a filter before measuring out an aliquot part.

M. J. S.

**Estimation of Arsenic and Phosphorus in Iron Ores.** By J. PATTINSON and H. S. PATTINSON (*J. Soc. Chem. Ind.*, 12, 119—121).—The authors recommend treating 3 grams of the ore with hydrochloric acid. After rendering the silica insoluble by evaporation, the residue is taken up with a very little acid, and then diluted with hot water to 50 c.c. A 50 per cent. solution of sodium thiosulphate is now run in until the iron is completely reduced to the ferrous state. The sulphurous acid is expelled by boiling, and, after cooling, 5 c.c. of strong hydrochloric acid is added. A little powdered zinc sulphide is now introduced, which causes the precipitation of any arsenic as trisulphide. The precipitate is first washed with hot 5 per cent. hydrochloric acid to remove any lead, and, after washing with water, it is digested with ammonium sulphide. The solution is evaporated to dryness on the water bath, the residue oxidised with bromine and a little nitric acid, and the arsenic finally precipitated, and weighed, as magnesium ammonium arsenate. The filtrate from the arsenic trisulphide is boiled to expel hydrogen sulphide, and diluted to 250 c.c.; a little ferric chloride is added, and the liquid neutralised with calcium carbonate. This will cause a precipitate of ferric phosphate, which must be washed on a filter with lukewarm water. To estimate the phosphorus, it must be dissolved in dilute nitric acid, and heated with solution of ammonium molybdate; this causes the precipitation of ammonium phosphomolybdate, which is then collected and weighed. The test analyses are certainly extremely satisfactory,

but, as no silicates were introduced, no evaporation to dryness in presence of hydrochloric acid was required, and therefore there could be no loss of arsenic.

L. DE K.

**Estimation of Boric acid in Boronatrocalcite.** By G. A. LE ROY (*Chem. Centr.*, 1893, ii, 291; from *Dull Soc. ind. Rouen*, 21, 62).—2.5–5 grams of the finely-powdered substance is decomposed in a reflux apparatus with a few c.c. of sulphuric acid diluted with an equal volume of water. The presence of a small quantity of hydrochloric acid facilitates the decomposition. The cooled mixture is filtered, the filter washed with acidified water, the filtrate neutralised with soda, heated to boiling, and again filtered. The filtrate is acidified with hydrochloric acid, boiled to expel carbonic anhydride, and then made up to a known bulk with water free from carbonic acid. The solution contains free boric acid and alkali sulphate and chloride.

20 c.c. of the solution is placed by the side of the same bulk of water, and an equal number of drops of a 10 per cent. solution of Poirrier's Orange III added to each. The acid solution is then titrated with a solution of sodium hydroxide until it acquires the same colour as the aqueous solution of the indicator. This titration gives the quantity of free hydrochloric acid. A second 20 c.c. of the acid solution is titrated with sodium hydroxide in the presence of Orange II until it acquires a dark-red colour. The difference in the two titrations gives the quantity of boric acid. The sodium hydroxide must be free from carbonates, silicates, and aluminates.

E. C. R.

**Analysis of Silicon Carbide.** By O. MÜHLHAUSER (*Zeit anal. Chem.*, 32, 564–567).—The analysis of this substance, which is being produced in America as a substitute for emery and bort under the name "Carborundum," presents peculiar difficulties, in consequence of its extreme hardness. After trituration in an agate mortar, it is necessary to submit the powder to elutriation, and accurate results in the carbon determination can only be obtained with that which remains in suspension for at least five minutes. The carbon is best estimated by combustion with 20 parts of lead chromate (the addition of potassium dichromate causing the oxidation to proceed with explosive rapidity); the silicon by fusion with potassium sodium carbonate for about six hours, during which the heat should be raised very gradually. A very pure specimen gave the following numbers:—C 30.2, Si 69.1 (Al, Fe)<sub>2</sub>O<sub>3</sub> 0.46, CaO 0.15, MgO 0.09 per cent. The formula SiC requires 30 per cent. of carbon.

M. J. S.

**Estimation of Copper as Cuprous Sulphide.** By R. WEGSCHEIDER (*Monatsh.*, 14, 315–322).—The author has found that in order to obtain accurate results in estimating copper as cuprous sulphide by heating the precipitated cupric sulphide in a current of hydrogen, the temperature must not be allowed to rise too high. A temperature of about 650° (dull red heat) is the highest which can be safely employed, as at higher temperatures than this a portion of the sulphide is reduced to metallic copper, hydrogen sulphide

being evolved. The substitution of coal-gas for hydrogen does not give good results. When hydrogen sulphide is employed instead of hydrogen, a portion of the cupric sulphide remains unreduced.

A. H.

**Separation of Metals in Alkaline Solution by means of Hydrogen Peroxide.** By P. JANNASCH (*Ber.*, 26, 2329—2331; compare Abstr., 1893, ii, 492).—Copper peroxide is precipitated on adding hydrogen peroxide to a solution of cupric hydroxide in dilute ammonia, but the reaction does not occur in presence of even slight excess of ammonia or ammonium salts. The precipitation is, in any case, incomplete, 1·5—2 per cent. of copper remaining dissolved. Copper peroxide forms voluminous, dark olive-green flocks, and appears to attack porcelain, as it was always found to contain silica. It is possible, by the help of hydrogen peroxide, to show in one solution the various oxidation stages of copper. On mixing 10 per cent. copper sulphate solution (3 c.c.) with 20 per cent. soda (4 c.c.), cupric hydroxide is precipitated; this is dissolved in 10 per cent. tartaric acid (3 c.c.) and 2 per cent. hydrogen peroxide solution (15 c.c.) added; copper peroxide is precipitated, but dissolves on heating, and on cooling the solution, cuprous oxide is deposited.

J. B. T.

**Separation of Metals in Alkaline Solution by means of Hydrogen Peroxide.** By P. JANNASCH and J. LESINSKY (*Ber.*, 26, 2331—2334, 2334—2336; compare preceding abstract).—*Separation of Lead from Copper.*—Lead nitrate (0·5 gram) and copper (0·3 gram) are dissolved in water (40 c.c.) and concentrated nitric acid (10 c.c.), and the solution treated at ordinary temperatures with a mixture (80—125 c.c.) of 3 parts of hydrogen peroxide (2 per cent.) and 1 part of strong ammonia. Saturated solution of ammonium carbonate (5 c.c.) is added, and the precipitate is washed 4 or 5 times with a mixture of hydrogen peroxide (1 part), concentrated ammonia (1 part), and water (6—8 parts); when all the copper is separated, the washing is continued with dilute ammonia (1:8) at 60—80°, and finally with warm water, in which the lead hydroxide is completely insoluble. The lead precipitate is dried and treated in the manner previously described (Abstr., 1893, ii, 493). The copper in the filtrate is determined in the usual manner, with due regard to the presence in the solution of nitric acid and ammonium salts. A large excess of hydrogen peroxide causes the lead to be precipitated in dense, crystalline plates. Mixtures of lead nitrate and copper sulphate may be separated in a similar manner if the precipitation of lead sulphate is prevented by the addition of acetic acid and ammonia. The analytical results agree closely with the theoretical.

*Separation of Lead from Zinc.*—Lead nitrate (0·5 gram) and zinc oxide (0·2 gram) are dissolved in concentrated nitric acid (2 c.c.) and water (50 c.c.); the solution is treated with a mixture of 2—3 per cent. hydrogen peroxide (40 c.c.) and concentrated ammonia (15 c.c.); saturated ammonium carbonate solution (5 c.c.) is then added, and the liquid well stirred, the lead oxide is collected, washed first with dilute ammonia and finally with cold water, and treated in the manner already described (*loc. cit.*). The concentrated filtrate

is treated with pure sodium hydroxide (5 grams) and boiled until free from ammonia; it is then acidified with hydrochloric acid, and the zinc precipitated with sodium carbonate and determined in the usual manner, care being taken to free it from silica or alumina. The lead oxide may also be precipitated in the crystalline form (see above).

*Separation of Lead from Nickel.*—Lead nitrate (0.5 gram) and potassium nickel sulphate (0.4 gram) are dissolved in concentrated nitric acid (5 c.c.) and water (50 c.c.), glacial acetic acid (5 c.c.) and strong ammonia (15 c.c.) are then added, and the lead precipitated with a mixture of hydrogen peroxide (75 c.c.) and concentrated ammonia (20 c.c.); the addition of ammonium carbonate is unnecessary. The lead oxide is precipitated in a flocculent condition, and is treated in the manner described in the separation of lead from copper (see above). The solution containing the nickel is evaporated to dryness, treated with concentrated hydrochloric acid (15 c.c.), evaporated to dryness again, the residue dissolved in dilute hydrochloric acid, the silica separated; the filtrate (250—300 c.c.) is then boiled, treated with aqueous hydroxylamine hydrochloride (4 grams), and precipitated with 15 per cent. soda (60—70 c.c.) in the usual manner. Hydroxylamine, in contradistinction to ammonia, causes the nickel to be precipitated in a form which admits of rapid filtration. The numerical results show a tolerably close agreement with the theoretical.

J. B. T.

**Estimation of Manganese by means of Potassium Permanganate.** By A. GORGEU (*Bull. Soc. Chim.*, [3], 9, 490—496).—When manganese is estimated, as in Guyard's method, by adding a solution of potassium permanganate to an almost neutral solution of manganous chloride, heated at 80°, the results are too low, partly in consequence of the acidity of the liquid. Donath's modification, in which the solution of the manganous salt is added to a solution of the permanganate mixed with sodium carbonate, also gives inexact results, unless the solutions are mixed very slowly, especially towards the end of the reaction. If Guyard's process is modified by adding precipitated calcium carbonate before the permanganate, the results are less exact than by Donath's method.

According to Guyard, three manganese permanganates,  $Mn_2O_{10}$ ,  $Mn_2O_{11}$ , and  $Mn_2O_{12}$ , can be obtained by mixing potassium permanganate and manganous chloride in different proportions. He seems, however, to have overlooked the fact that hydrogen chloride is liberated at the same time. The author finds that the oxide  $Mn_2O_{11}$  is never formed, even when the liquid is kept neutral, and the two oxides  $Mn_2O_{11}$  and  $Mn_2O_{10}$  are only formed when the acid that is set free is continually neutralised with calcium carbonate. The author criticises Guyard's views as to the constitution of these oxides, and contends that there is no evidence that they are manganese permanganates, and also that Guyard has advanced no evidence of the existence of manganese manganates.

C. H. B.

**Estimation of Oxide of Iron and Alumina in Mineral Phosphates.** By A. SMETHAM (*J. Soc. Chem. Ind.*, 12, 112—116).—The author uses Glaser's process, and checks the results by his ammonium acetate method. The analyses should agree within 0.1 per cent. The ammonium acetate process is carried out as follows:—2 grams of the sample is evaporated with strong hydrochloric acid, and the residue is taken up with 10 c.c. of dilute acid, and filtered from any siliceous residues. After boiling with a few drops of bromine, the liquid is allowed to cool, and mixed with dilute ammonia until a permanent precipitate is produced, which is then again dissolved by cautious addition of hydrochloric acid. Large excess of ammonium acetate is now added, and the precipitate is collected on a filter, well washed, burnt, and weighed. It theoretically consists of ferric and aluminium phosphates, but in practice it will be found to contain variable quantities of calcium phosphate. It must, therefore, be quantitatively tested for phosphoric anhydride, calcium oxide, and ferric oxide; the alumina then being found by difference. The author conducts the analysis as follows:—The precipitate is dissolved in hydrochloric acid, diluted with water, and, after adding some citric acid, boiled with ammonium oxalate. Dilute ammonia is then added until the liquid is neutral to litmus paper, and subsequently acetic acid to slightly acid reaction. The calcium oxalate is collected after some time, and ignited to carbonate as usual. The filtrate from the lime is mixed with magnesia mixture, the precipitate being afterwards purified by redissolving and reprecipitating, and from the filtrate from the magnesium ammonium phosphate, the iron is precipitated with ammonium sulphide and treated as usual. The calcium carbonate is calculated to oxide; the magnesium pyrophosphate to phosphoric anhydride; to their sum is added the weight of the ferric oxide, and the deficiency represents the alumina. L. DE K.

**Electrolytic Estimations and Separations.** By G. VORTMANN (*Monatsh.*, 14, 536—552).—The author describes the behaviour on electrolysis of salts of zinc, iron, cobalt, and nickel, to which solutions of an alkaline tartrate and an alkaline hydroxide have been previously added. Of these metals, the three first named may be quantitatively deposited from the alkaline solution; whilst, under the same conditions, the last named remains in solution, thus affording a method for the separation of nickel from zinc, iron, and cobalt. Iron may be separated from zinc in alkaline tartrate solution by employing a cathode of platinum, whereby the iron is deposited with only a trace of zinc. By dissolving and redepositing two or three times, the iron is obtained entirely free from zinc. To estimate zinc in presence of iron, potassium cyanide is first added to the solution, whereby the iron is converted into potassium ferrocyanide; sodium hydroxide is then added and the current passed, when the zinc is deposited, the iron remaining in solution.

The author further describes a method of estimating cobalt, nickel, and copper when present with much iron. A solution of the metal, in which the iron is present as a ferric salt, is placed in a platinum dish and treated with excess of ammonia, and the current passed, where-

upon, without the necessity of filtering off the ferric hydroxide, cobalt, nickel, and copper are thrown down on the cathode in a well-adhering mass. In the separation of copper and iron, the latter metal is best oxidised with nitric acid. G. T. M.

**Separation of Nickel from Cobalt.** By H. HERRENSCHWIDT and E. CAPELLE (*Zeit. anal. Chem.*, 32, 607—610; from *Le Cobalt et le Nickel*, Rouen, 1888).—The potassium nitrite process is not capable of giving a complete separation. Traces of nickel can be detected in presence of much cobalt by microscopic examination, in consequence of the different colours of cobaltic and nickelic hydroxides, that of cobalt being a pale brown, whilst nickelic hydroxide is black. On examining, with a magnifying power of 180 to 200 diameters, the precipitate thrown down by excess of sodium hypochlorite from the nearly neutralised solution, a completely black field will be seen if the nickel amounts to 1 per cent. of the cobalt, but when only traces are present, they are exhibited as black spots on a brown field. Traces of cobalt can be separated from much nickel by suspending the hydroxides in water or an alkali, and passing chlorine, when the nickel dissolves completely, the cobalt remaining undissolved. The practical method of estimating the two metals in ores, &c., is, therefore, as follows:—After removal of the metals precipitable by hydrogen sulphide and ammonium carbonate, an excess of ammonium sulphide is added, then a small excess of acetic acid, and the liquid is boiled. The precipitate is rapidly filtered off, and washed with hot ammonium acetate. It is then dissolved in nitric acid, the solution evaporated to dryness, taken up with water, filtered from sulphur, and divided into two parts. One part is evaporated with sulphuric acid, ignited very gently, and the residue of metallic sulphates weighed. The other half is treated with potassium cyanide and bromine, and the well-washed precipitate treated with chlorine. The solution containing the nickel is feebly acidified with hydrochloric acid, boiled to expel chlorine, and poured into boiling soda. The precipitate is washed, dissolved in hydrochloric acid, and converted into sulphate, as above, for weighing. When zinc is present, the mixed sulphates of nickel and zinc are dissolved, and the metals precipitated by hydrogen sulphide, after adding ammonium acetate and acetic acid. The precipitate is treated with dilute hydrochloric acid, potassium cyanide added to the neutralised solution, and the zinc thrown down by potassium sulphide and weighed. The corresponding quantity of sulphate is deducted from the weight of the mixed sulphates.

M. J. S.

**Estimation of Chromium in Ferrochromium and Steel.** By J. CLARK (*J. Soc. Chem. Ind.*, 11, 501—504; 12, 340—341).—Finely pulverised ferrochromium, if rich in chromium, is very readily oxidised when heated with a mixture of magnesia and sodium hydroxide (2 parts of the former to 3 of the latter). The crucible containing the intimate mixture is heated for half an hour with the tip of a small bunsen burner flame, and subsequently for another half hour to dull redness. The contents are then boiled with water, hydrogen



peroxide is added to reduce any manganate, and, after boiling for some minutes, the solution is filtered. The insoluble matter may still contain chromium. It should be ignited, ground in an agate mortar, and again fused with the magnesia-soda mixture, and this fusion may even need to be repeated a third time. The solutions are acidified with sulphuric acid, and the chromic acid titrated by Penny's process. For poor alloys, ignition in a porcelain crucible over the blowpipe or in a muffle with 3 parts of calcium hydroxide should precede the ignition with magnesia-soda mixture. In this case about 3 parts of sodium hydrogen carbonate should be added to the solution before filtration, for the purpose of removing the calcium. Second and third fusions are required in this method also. The powdered ferrochromium may also be prepared for the fusion with magnesia-soda by a preliminary heating in sulphur vapour, or, better, vapour of carbon bisulphide, in a boat in a porcelain tube. The sulphides produced are very bulky, and, in the case of sulphur, a slight loss results from the violence of the action. The sulphides may be at once mixed with 8 parts of magnesia-soda, or be first roasted in a porcelain crucible, and then fused with 5 parts of the mixture.

Chromium steel is best attacked by the carbon bisulphide method. The residue from the first fusion with magnesia-soda will usually yield a very small amount of chromate on a second fusion. In cases where the alloy can be dissolved in dilute hydrochloric acid, the solution is treated with ammonia until a permanent precipitate is produced, and then with a small excess of sodium phosphate and about double that amount of sodium thiosulphate or, preferably, sulphite, and boiled for 10 minutes. The precipitate, which contains all the chromium, is washed, gently ignited, ground, and fused with 8 parts of magnesia-soda. Equally good results are obtained when the hydrochloric acid solution is neutralised with sodium carbonate, and boiled with sodium sulphite as long as sulphurous anhydride comes off. The precipitate, which contains all the chromium as basic sulphite, is ignited and fused as above.

M. J. S.

**Estimation of Cyanides in Gas Refuse.** By W. LEYBOLD (*Zeit. anal. Chem.*, 32, 571—572).—The powdered substance is treated with soda to convert the cyanide into ferrocyanide, and a portion of the solution is evaporated to dryness with excess of sulphuric acid, and heated until the excess of acid is expelled. The ferric sulphate which remains is dissolved in sulphuric acid, reduced with zinc, and titrated with permanganate.

A possible objection that, in the presence of organic matter, iron might be dissolved by the alkali in other forms than as ferrocyanide, is met by the consideration that there is always formed at the same time an alkaline sulphide, by which such iron would be precipitated.

M. J. S.

## General and Physical Chemistry.

**Refractive Indices of Liquid Nitrogen and of Air.** By G. D. LIVING and J. DEWAR (*Phil. Mag.*, [5], 36, 328—331).—The authors have determined the refractive indices of liquid nitrogen and air, using Terquem and Trannin's method of suspending in the liquid two parallel glass plates with a thin layer of air between them, and measuring the angle of incidence at which the ray suffers total reflection at the surface of the air. The liquid nitrogen was contained in a vacuum-jacketed tube, the liquid acting as a lens, and the source of light and the spectroscopic-slit being conjugate foci when the liquid was midway between them. The glass plates were separated by a ring of thin filter-paper, thoroughly wetted with white of egg, and allowed to dry, and were attached to a rod which formed the prolongation of the vertical axis of a theodolite used to measure the angle through which they were turned.

The apparatus gave for liquid oxygen,  $\mu_D = 1.226$ , slightly larger than the value obtained by the authors with a prism, namely, 1.2236.

For nitrogen which contained 5 per cent. of oxygen, the refractive index was found to be  $\mu_D = 1.2053$  at  $-190^\circ$ , and for air,  $\mu_D = 1.2062$ .

The refraction constant for liquid nitrogen, according to Gladstone's formula, is 0.225, and the refraction equivalent, 3.153; according to Lorenz's formula, these values become 0.1474 and 2.063 respectively.

J. W.

**Polarisation of Platinum Electrodes in Sulphuric acid.** By J. B. HENDERSON (*Proc. Roy. Soc.*, 54, 77—82).—Of two platinum electrodes immersed in sulphuric acid and connected with the primary circuit, one was also connected with the earth, and the other through a key with one pair of quadrants of an electrometer. Connected with the same pair of quadrants, through another key, was the slider on a bridge with a special battery. The other pair of quadrants and one end of the bridge were earthed. The slider was so moved that the permanent deflection it gave on the electrometer was not disturbed when the primary circuit was broken and the polarised electrodes connected with the instrument. The potential of the quadrants was then that of the polarisation. The mean value of the electromotive force of polarisation determined in this way was 2.09 volts, the primary current varying from 0.2 to 1.0 amp., the time of its passing from 25 minutes to 18 hours, and the strength of the solutions from 5 to 30 per cent. The extreme values were 2.05 and 2.14.

J. W.

**Use of Cupric Nitrate in the Voltameter and the Electrochemical Equivalent of Copper.** By F. E. BEACH (*Amer. J. Sci.*, [3], 46, 81—88).—The object of this paper is to show that cupric nitrate has some marked advantages over the sulphate for use in the voltameter. The nitrate solution freshly prepared has a tendency to dissolve copper, which decreases, however, after the copper

electrode has been kept in the solution for a sufficient length of time. Another difficulty is due to oxidation of the copper deposited, which may be prevented by the addition of a small amount of ammonium chloride. The following method is recommended for the preparation of the solution:—Dissolve copper nitrate, the purest obtainable, in distilled water. Boil for a short time to expel the air, and keep at a temperature of 100° for an hour or two in the presence of bright metallic copper in order to completely neutralise the solution. When ready for use, it should have a density of about 1.53. Add a saturated solution of ammonium chloride at about the rate of 1 drop to 100 c.c. of the nitrate. It is not easy to specify the proper amount of ammonium chloride necessary, and the surest way is to try a preliminary experiment. If too much be present, the deposit will discolour on drying; if too little, the deposit will oxidise in the solution. The weight of copper deposited does not appear to depend on the current density, and is practically independent of the temperature between 10° and 35°.

The equivalent obtained for copper, using the nitrate, agrees very well with that calculated from the best chemical determinations.

H. C.

**Ratio of the Specific Heats of Paraffins, &c.** By J. W. CAPSTICK (*Proc. Roy. Soc.*, 54, 101—104).—The ratio of the specific heats at constant volume and constant pressure of several gaseous paraffins and their halogen derivatives at the ordinary temperature was calculated from the velocity of sound in the gases obtained by using Kundt's method. The mean values of the ratio are as follows:—Methane, 1.313; methylic chloride, 1.279; methylic bromide, 1.274; methylic iodide, 1.286. Ethane, 1.182; ethylic chloride, 1.187; ethylic bromide, 1.188. Propane, 1.130; propylic chloride, 1.126; isopropylic chloride, 1.127; isopropylic bromide, 1.131.

It will be noticed that these ratios fall into four groups: (a) methane, (b) methylic haloids, (c) ethane and its derivatives, (d) propane and its derivatives, the ratio for each group being constant.

A form of vapour density apparatus, giving results concordant to 0.1 per cent., is described in the paper.

J. W.

**Thermal Properties of a Mixture of Carbonic Anhydride and Nitrogen.** By K. TSURUTA (*Phil. Mag.*, [5], 36, 438—453).—The author has calculated from Andrews' observations the isothermals, isometrics, and isopiestic of a mixture of carbonic anhydride and nitrogen in the proportion of 3 to 4. He uses Clausius' equation

$$p = \frac{RT}{v - \alpha} - \frac{K}{T(v + \beta)^2},$$

adopting Margules' values for the constants B, K,  $\alpha$ ,  $\beta$ . The results are given in tabular and curve form.

J. W.

**Dissociation Pressure and the Individuality of Chemical Compounds.** By V. KURILOFF (*J. Russ. Chem. Soc.*, 25, 170—192).—The author has studied the variation of the vapour pressure of ammonia with varying concentration in the liquid first obtained by Divers by passing ammonia over ammonium nitrate. The liquid behaves as if it were a solution of ammonium nitrate in ammonia,

the vapour pressure decreasing as ammonia is removed, until the solid begins to separate out, after which it remains constant, until the whole has become solid. The solubility of the ammonium nitrate in ammonia increases with rise of temperature.

Similar experiments were made with the liquid obtained by passing ammonia over ammonium bromide. The solution in this case seems to be one of the compound  $\text{NH}_4\text{Br}, \text{NH}_3$  in ammonia. So long as solid and liquid are present together, the vapour pressure again remains constant.

Care must be taken, therefore, in drawing conclusions as to the individuality of substances from the constancy of their vapour pressure. This constancy may be due to the existence of an individual compound, but it may also arise from the presence of a heterogeneous mixed system.

J. W.

**Supersaturated Solutions.** By A. L. POTILITZIN (*J. Russ. Chem. Soc.*, 25, 201—207).—The author has stated (Abstr., 1893, ii, 509) that salts containing water of crystallisation which do not decompose at the ordinary temperature in dry air or in a vacuum, or decompose only very slowly, are incapable at that temperature of forming supersaturated solutions. The hydrated salt  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  is apparently an exception to this rule, as it does not lose water at the ordinary temperature, and still can give supersaturated solutions. This the author explains by assuming that the hydrate  $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$ , which is more soluble than the hydrate  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , exists in the solution at the ordinary temperature, and only changes slowly into the dihydrate.

J. W.

**Distillation in a Vacuum.** By A. ANGELI (*Gazzetta*, 23, ii, 104).—In the distillation of small quantities of liquid under diminished pressure, very good results are obtained by almost filling the distillation flask with glass wool.

W. J. P.

## Inorganic Chemistry.

**True Atomic Weight of Hydrogen.** By G. HINRICHS (*Compt. rend.*, 117, 663—666).—The author has applied his method of limits (Abstr., 1893, ii, 316) to the results of Keiser, Cooke and Richards, Dittmar and Henderson, and Morley, making use of some hitherto unpublished data supplied by the last. The application is somewhat difficult, because in each series of experiments the weight of materials employed has varied but little. It is clear, however, that the divergencies from the value  $\text{H} = 1$  are functions of the weight of hydrogen employed, and if equal weight is attached to the work of Dittmar, Keiser, and Morley, the divergencies from this value fall

on a curve which is represented by the formula  $\eta = \frac{h}{5000} (5^3 - h^3)$ , where  $h$  is the weight of hydrogen and  $\eta$  the divergence from unity.

For the limit  $h = 0$ ,  $\eta = 0$ , and hence  $H = 1$  exactly when  $O = 16$  (compare *loc. cit.*). C. H. B.

**Relation between the Precipitation of Chlorides by Hydrochloric acid and the Reduction of the Freezing Point.** By R. ENGEL (*Compt. rend.*, 117, 485—488).—The law that 1 mol. of hydrochloric acid will precipitate from its saturated solution at  $0^\circ$  1 atom of chlorine in the form of the chloride of a univalent or bivalent metal holds good for temperatures as high as  $75^\circ$ .

The law also holds good for the double chloride  $\text{CuCl}_2 \cdot 2\text{NH}_4\text{Cl}$ , 1 mol. of which is precipitated by 4 mols. of hydrochloric acid.

Van't Hoff has shown that the molecular osmotic pressure of hydrochloric acid, 1.98, is practically the same as that of sodium chloride, 1.89, and therefore 1 mol. of the acid should precipitate 1.05 mol. of the salt. In the case of the chlorides of bivalent metals, the molecular reduction of the freezing point is not double that of the chlorides of univalent metals. The author finds, however, that the molecular reduction produced by chlorides of univalent metals remains practically the same for various concentrations, and for different chlorides varies only between 35 and 40. With chlorides of bivalent metals, on the contrary, the molecular reduction increases with the concentration and becomes practically double that of the univalent chlorides. The molecular reduction of the double salt  $\text{CuCl}_2 \cdot 2\text{NH}_4\text{Cl}$  also increases with the concentration and tends to become four times as great as that of univalent chlorides. The following table shows the relation between the nature of the chloride, the molecular reduction of the freezing point, and the number of molecules of hydrochloric acid required to precipitate 1 mol. of the salt.

	Atoms of chlorine in the molecule.	Ratio of the molecular reductions.	Mols. HCl.
Chlorides of univalent metals ..	1	1	1
"          bivalent ..	2	2	2
Double chloride, $\text{CuCl}_2 \cdot 2\text{NH}_4\text{Cl}$ ..	4	4	4

In this connection, it is important to observe, however, that sodium hydroxide, which has practically the same molecular osmotic pressure as hydrochloric acid, precipitates only  $\frac{1}{2}$  mol. of sodium chloride, bromide, or iodide from a saturated solution.

When the number of molecules of water in combination with a molecule of a chloride at the freezing point of its saturated solution is calculated, it appears that the product of this number into the reduction of temperature is a constant which has double the value in the case of chlorides of bivalent metals that it has in the case of chlorides of univalent metals.

	Molecules of water.	Freezing point.	Product.
Ammonium chloride.....	12.4	15.5	19.2
Potassium chloride.....	16.6	11.4	18.9
Potassium iodide .....	8.5	22.0	18.7

	Molecules of water.	Freezing point.	Product.
Sodium bromide.....	8.1	24.0	19.4
Ammonium iodide .....	6.4	27.5	17.6
Strontium chloride.....	22.9	17.0	38.9
Calcium chloride .....	10.7	37.0	39.6

C. H. B.

**Ozone.** By A. WOLKOWICZ (*Zeit. anorg. Chem.*, 5, 264—265).—From a consideration of the position of oxygen in the periodic system, it is concluded that ozone has the constitution  $O_3O$ , just as sulphurous anhydride is  $O_2S$ . Ozone would then be the anhydride of an acid  $H_2O_3$ , corresponding with  $H_2SO_3$ . This acid, like sulphurous acid, is unknown, but potassium tetroxide,  $K_2O_4$ , is its potassium salt, and resembles the sulphite in its property of reducing permanganate.

C. F. B.

**Decomposition of Nitrous acid in Nitric acid Solution.** By B. LILJENSZTERN and L. MARCHLEWSKI (*Zeit. anorg. Chem.*, 5, 288—292).—By passing a stream of carbonic anhydride through 60 per cent. nitric acid to which 4 per cent. of nitric peroxide had been added, and determining the ratio of nitrous to total nitrogen in the gases carried over, it was shown that the nitric acid contained nitrous acid in addition to nitric peroxide. Montemartini's statement (*Real. Accad. Linc.*, 1, 63), that the reaction  $HNO_2 + HNO_3 = 2NO_2 + H_2O$  is the only one that takes place in nitric acid of over 30 per cent. strength, is, therefore, erroneous.

C. F. B.

**Conversion of Yellow Phosphorus into Red Phosphorus.** By J. W. RETGERS (*Zeit. anorg. Chem.*, 5, 211—230; compare Pedler, *Trans.*, 1890, 599; Retgers, *Abstr.*, 1893, ii, 457; Muthmann, *ibid.*, 458).—It is generally admitted that yellow phosphorus crystallises from the usual organic solvents in dodecahedra; the crystals are best obtained by cooling a hot solution. The author cannot substantiate the text-book statement that yellow phosphorus crystallises from essential oils in octahedra. Thus, whilst it is admitted that yellow phosphorus is crystalline, this substance has, on several occasions, been described as amorphous. This is not surprising in view of the fact that a thin layer of yellow phosphorus between two thin glasses has all the appearance of an amorphous substance.

When phosphorus is heated, it passes through three stages:—(1) it becomes yellow to brown, but remains transparent and regular; (2) a granular, undoubtedly crystalline, segregation occurs (formation of red, opaque phosphorus); (3) a graphitic, chocolate-coloured phosphorus is produced. The second stage corresponds with the first production of a true modification.

The same series of changes is produced by light—not merely superficially, as stated in text-books—a fact which the author calls in evidence of his contention that red phosphorus is not amorphous.

The author has not been able to determine the character of the white crust which forms on phosphorus which has been submerged

in water, but he inclines towards the opinion that it is a hydrate rather than a modification.

It is pointed out that the properties of an amorphous modification are never intermediate between those of two crystalline modifications. If red phosphorus were amorphous, this rule would be violated; for the specific gravity of red phosphorus is 2.148, whilst that of regular, yellow phosphorus is 1.826, and that of chocolate-coloured, hexagonal phosphorus is 2.34.

Some remarks in reply to Muthmann (Abstr., 1893, ii, 458) are included in the paper. A. G. B.

**Volatility of Pyrophosphoric acid.** By G. WATSON (*Chem. News*, 68, 199—200).—The author has made a series of experiments, heating weighed quantities of orthophosphoric acid for various periods, at fixed temperatures, and examining the products; from which he concludes that orthophosphoric acid requires a temperature above 230—235° for its complete dehydration into pyrophosphoric acid; that at 255—260° it is completely converted into pyrophosphoric acid, which is, moreover, volatile at that temperature; that at 290—300° metaphosphoric acid is beginning to form. D. A. L.

**Action of the Electric Arc on the Diamond, Amorphous Boron, and Crystallised Silicon.** By H. MOISSAN (*Compt. rend.*, 117, 423—425).—In the electric arc, at a somewhat high temperature, the diamond becomes incandescent, swells up without melting, and becomes covered with black masses, consisting entirely of hexagonal lamellæ of graphite, which is easily converted into graphitic oxide. If the diamond is placed in a small carbon crucible in the electric furnace previously described, and is subjected to the action of an arc produced by a current of 70 volts and 400 ampères, the crystal first breaks up into small fragments along the planes of cleavage, and then at a higher temperature swells up and is completely converted into graphite, which yields yellow graphitic oxide. It follows that at the temperature of even a moderately intense electric arc, the stable form of carbon is graphite. When heated in a carbon envelope at the temperature of the oxy-hydrogen blow-pipe, the diamond is sometimes covered with an adherent black mass, which slowly dissolves in a mixture of potassium chlorate and nitric acid, but which is not graphite.

Amorphous boron, prepared by means of magnesium, volatilises without fusion in the electric arc, the extremities of the electrodes being converted into partially-crystallised boron carbide.

Crystallised silicon, when heated in the arc, first melts and then boils, the extremities of the electrodes at the end of the experiment being covered with pale green crystals of carbon silicide.

The phenomena in the arc were observed by projecting on a screen by means of an intense arc an image of the arc of lower intensity in which the substances were heated. C. H. B.

**Silicon Carbide.** By O. MÜHLHAUSER (*Zeit. anorg. Chem.*, 5, 105—125).—A mixture of finely-powdered coke, sand, and salt was

packed around a carbon core in an oblong fire-brick box. The core was connected with the terminals of a transformer, whereby it could be heated until the mixture surrounding it became white hot. A transverse section of the mass after the reaction showed that the core was surrounded by (a) a zone of adhering graphite, (b) a zone of crystalline silicon carbide, (c) a zone of amorphous silicon carbide, (d) a zone containing pockets of fibrous material, (e) a zone of the original mixture only slightly altered, and (f) a hard skin consisting almost entirely of salt.

The graphite has all the properties of the natural mineral, and the same crystalline form as that of the silicon carbide, a fact which indicates that the latter compound is at first formed in this zone and subsequently loses its silicon by volatilisation. The outer portion of this zone, when washed, left 33·71 per cent. of variously-coloured crystals, which contain 30·49 per cent. of silicon and 68·26 per cent. of carbon. These crystals differed considerably in appearance from those in the zone of silicon carbide; they were frequently parti-coloured, green, violet, and red being the prevailing tints.

The crystalline silicon carbide (*carborundum*) constituted the chief product of the reaction. The mass was easily broken up in a mortar, when the separate crystals were found to be bluish or yellowish-green; their size varied from a diameter of several millimetres to merely microscopic dimensions. The largest crystals occurred in fissures in the mass, where, apparently, there was room for them to form, and it remains an open question whether they had separated from a fused mass or were a product of sublimation.

To purify silicon carbide it may be heated to dull redness in oxygen, then boiled with potash solution, washed, digested with hydrochloric acid, again washed, and finally treated with hydrofluoric and sulphuric acids. After this treatment, its composition corresponds with the formula  $\text{SiC}$ .

Silicon carbide is insoluble in all acids, but is attacked by molten alkalis. It burns very slowly in oxygen when very finely divided, and if strongly heated in a platinum crucible it becomes a greenish-golden mass of great beauty, a portion of it being burnt during the ignition. It is attacked by hot ferric oxide. Its specific gravity at 15° is 3·22, but when finely divided it remains suspended in water for months.

The amorphous silicon carbide found in the third zone has all the properties of the crystalline specimens.

The fibrous material found in fissures and pockets in the fourth zone consists of silicon, aluminium, and carbon with a little lime and magnesia; it would thus appear to be a polycarbide of silicon and aluminium.

Much salt was volatilised during the reaction; the gas evolved consisted largely of carbon monoxide. A. G. B.

**Crystallised Carbon Silicide.** By H. MOISSAN (*Compt. rend.*, 117, 425—428).—When carbon is dissolved in fused silicon in a wind furnace, crystals of carbon silicide several mm. in length can be obtained, and it follows that the two elements combine readily in a



fused medium at 1200—1400°. The silicide can, however, be prepared much more easily by heating in an electric furnace a mixture of 12 parts of carbon and 28 parts of silicon, the product being first heated with a mixture of nitric and hydrofluoric acids, and afterwards with a mixture of nitric acid and potassium chlorate. As a rule, the crystals are yellow, but by operating in a closed crucible with silicon as free as possible from iron, transparent, sapphire-blue crystals are obtained.

If iron silicide is heated with excess of silicon in the electric furnace, and the product is treated successively with aqua regia, nitric and hydrofluoric acids, and nitric acid and potassium chlorate, crystals of carbon silicide are obtained, and the result is similar with a mixture of iron, silicon, and carbon, or of iron, silica, and carbon.

The silicide is also produced by heating carbon and silica in the electric furnace, or by allowing the vapour of carbon to come into contact with vapour of silicon, when it is obtained in almost colourless, very hard and brittle, prismatic needles.

Carbon silicide prepared by any of these methods has the composition  $\text{CSi}$ , and is colourless when free from iron. It is very distinctly crystalline, and sometimes forms regular, hexagonal lamellæ, which occasionally, though very rarely, show triangular impressions and parallel striæ. They act strongly on polarised light. The crystals are very hard, and scratch chrome steel and rubies. Sp. gr. = 3.12.

Carbon silicide is not affected by oxygen at 1000°, nor when heated in air by a Schloesing's blowpipe. Sulphur vapour at 1000° is without action, and chlorine at 600° attacks the compound very slowly, although its action is complete at 1200°. Fused potassium nitrate or chlorate, boiling sulphuric, nitric, and hydrochloric acids, aqua regia, and mixtures of nitric and hydrofluoric acids do not attack it.

Fused lead chromate oxidises the silicide, but repeated treatment is necessary in order to obtain complete combustion of the carbon. Fused potassium hydroxide gradually converts it into potassium carbonate and silicate.

C. H. B.

**Volatility of Ammonium Chloride.** By K. KRAUT (*Zeit. anorg. Chem.*, 5, 278—279).—When ammonium chloride is heated in a platinum basin in a water bath, an appreciable amount is lost by volatilisation; 50 per cent. of the whole if the heating is continued for 270 hours.

C. F. B.

**Hemihydrate of Calcium Sulphate.** By A. L. POTILITZIN (*J. Russ. Chem. Soc.*, 25, 207—210).—The hydrate  $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$  may be formed by dehydrating gypsum at 98—99°, the water being lost very slowly; or it may be formed by exposing anhydrous calcium sulphate to the air. The absorption of moisture is at first rapid, but the rate soon diminishes. The hemihydrate is capable of taking up small quantities of moisture from the atmosphere, and large quantities when allowed to remain over water. This excess of water is only partially lost when the hydrate is placed over sulphuric acid.

J. W.

**Double Haloids of Cæsium with Zinc and Magnesium.** By H. L. WELLS and G. F. CAMPBELL (*Zeit. anorg. Chem.*, 5, 273—277).—The following salts were prepared, and crystallise in colourless prisms or plates.  $3\text{CsCl}, \text{ZnCl}_2$ ;  $3\text{CsBr}, \text{ZnBr}_2$ ;  $3\text{CsI}, \text{ZnI}_2$ ;  $2\text{CsCl}, \text{ZnCl}_2$ ;  $2\text{CsBr}, \text{ZnBr}_2$ ;  $2\text{CsI}, \text{ZnI}_2$ ;  $\text{CsCl}, \text{MgCl}_2 + 6\text{H}_2\text{O}$ ;  $\text{CsBr}, \text{MgBr}_2 + 6\text{H}_2\text{O}$ . Zinc probably also forms salts of the 1 : 1 type, but the solutions are so syrupy that pure crystals cannot be obtained.

No double chloride of cæsium and beryllium could be prepared.

C. F. B.

**Double Haloids of Cæsium and Cadmium.** By H. L. WELLS and P. T. WALDEN (*Zeit. anorg. Chem.*, 5, 266—272).—The following salts were prepared, and are all colourless.  $3\text{CsBr}, \text{CdBr}_2$ ;  $3\text{CsI}, \text{CdI}_2$ ;  $2\text{CsCl}, \text{CdCl}_2$ ;  $2\text{CsBr}, \text{CdBr}_2$ ;  $2\text{CsI}, \text{CdI}_2$ ;  $\text{CsCl}, \text{CdCl}_2$ ;  $\text{CsBr}, \text{CdBr}_2$ ;  $\text{CsI}, \text{CdI}_2 + \text{H}_2\text{O}$ . Those of the 1 : 1 type, and  $2\text{CsI}_2, \text{CdI}_2$ , can be recrystallised from water; the others, when so treated, yield generally salts of the 1 : 1 type.

C. F. B.

**Occlusion of Gases by Metallic Oxides.** By T. W. RICHARDS and E. F. ROGERS (*Amer. Chem. J.*, 15, 567—578).—As in the case of cupric oxide, the oxides of zinc and nickel, and especially of magnesium, when prepared by ignition of the nitrates, are found to contain occluded gas; but the oxides of cadmium, mercury, lead, and bismuth retain no gas when prepared in this way. No gas is in any case retained when the oxide is prepared by ignition of the carbonate. The occluded gas was liberated by dissolving the oxide in hydrochloric acid, and was measured and analysed; it consisted mainly of oxygen and nitrogen, together with a very small quantity of a gas that dissolved in caustic potash, and was assumed to be carbonic anhydride [no reason is, however, given why this gas should not have been an oxide of nitrogen]. Oxides which still contained a trace of nitrate were found to be devoid of occluded gas; hence this gas must, in the other cases, have been derived from the decomposition of the last trace of nitric acid. The amount retained varied with the physical nature of the oxides, the more compact oxides retaining more gas, whilst those which form very fine powders retained no gas at all.

This occlusion of gases affects the atomic weights of a number of elements of which the oxides, as prepared by ignition of the nitrates, have been used in determining the atomic weights.

C. F. B.

**Compounds of Hydroxylamine with Metallic Carbonates.** By H. GOLDSCHMIDT and K. L. SYNGROS (*Zeit. anorg. Chem.*, 5, 129—146).—*Dihydroxylamine zinc carbonate*,  $\text{Zn}(\text{NH}_2\text{O})_2\text{CO}_3$  is prepared by dissolving hydroxylamine hydrochloride and zinc chloride in water, adding an equivalent quantity of sodium carbonate, and passing air through the solution, when the new compound is precipitated. It is a white, microcrystalline powder, of sp. gr. 2.50 at 18°, insoluble in water. The function of the air in the above method of preparation is to remove carbonic anhydride from the solution. Cryoscopic experiments indicate that the zinc exists in the solution partly as the ion  $\text{Zn}(\text{NH}_2\text{O})_2$ , and partly as dissociated zinc hydrogen carbonate;

the removal of a portion of the carbonic anhydride determines the molecular rearrangement.

When sodium carbonate solution is added to a solution containing ferrous chloride and hydroxylamine hydrochloride, a dark red coloration is produced, and the passage of hydrogen through the liquid determines the formation of a nearly black precipitate which contains ferrous oxide, hydroxylamine, and carbonic anhydride, but cannot be dried without decomposition. A cryoscopic examination of the solution indicates the presence of the ion  $\text{Fe}(\text{NH}_2\text{O})_2$ .

When manganous chloride is mixed with hydroxylamine hydrochloride and sodium carbonate, a slight precipitate is first formed; this was filtered off, and a current of air was passed through the solution. A nearly white precipitate was thrown down, which dried to a grey powder, having the composition  $4\text{MnCO}_3 \cdot 3\text{NH}_2\text{O} \cdot 2\text{H}_2\text{O}$ . A cryoscopic investigation showed that in this case no complex ion of metal and hydroxylamine exists in the solution.

The precipitate obtained by similar treatment of nickelous chloride varies in composition with the time during which air is passed through the liquid, and in no case is it of a very definite character.

Cadmium chloride gives a slight precipitate when mixed with hydroxylamine hydrochloride and sodium carbonate in solution, and when this has been filtered, the filtrate spontaneously deposits the dihydroxylamine cadmium chloride,  $\text{Cd}(\text{NH}_2\text{O})_2\text{Cl}_2$ , previously prepared by L. de Bruyn and Crismer (*Abstr.*, 1890, 558). This is somewhat soluble in cold water, and crystallises from hot water in white prisms; its sp. gr. is 2.72 at 18°. A. G. B.

**Preparation of Anhydrous Crystalline Metallic Silicates.** By H. TRAUBE (*Ber.*, 26, 2735—2736).—When amorphous zinc silicate, prepared by precipitating a solution of zinc sulphate with sodium silicate, is heated with boric acid for 10 days at a high temperature, it is converted into a white, crystalline powder, which has the composition  $\text{ZnSiO}_3$ , and is insoluble in acids. The optical properties of the crystals show that they belong to the rhombic system, and the product is therefore a zinc-pyroxene isomorphous with the mineral enstatite. E. C. R.

**Lead Oxide as a Mordant.** By A. BONNET (*Compt. rend.*, 117, 518—519).—When cotton is mordanted with an alkali plumbate and then washed with a large quantity of water, dissociation takes place, and the fibre becomes charged with lead peroxide, which partially oxidises and destroys it. A similar change takes place with plumbites, except that the fibre is not oxidised, lead monoxide being deposited. If the fibre thus treated is immersed in solutions of campeachy wood, it is dyed black; with shumac, it becomes green; with old fustic, a bright yellow. Tannin and catechu are also strongly attracted.

By immersing the tissue thus mordanted with lead oxide in hot neutral solutions of other salts, the tissue can be impregnated in a similar manner with oxides of gold, silver, mercury, vanadium,

manganese, chromium, iron, cobalt, nickel, and zinc, double decomposition taking place, and a lead salt going into solution.

C. H. B.

**The True Atomic Weight of Copper.** By G. HINRICHS (*Zeit. anorg. Chem.*, 5, 293—298).—A protest against alleged errors in the atomic weight determinations of Stas and his followers, a recent determination by Richards of the atomic weight of copper (Abstr., 1893, ii, 12) being selected as a specimen of such faulty methods.

[In the opinion of the abstractor, the author does not substantiate all his objections, and the alternative "method of limits" which he proposes seems open to damaging criticism.]

C. F. B.

**Colour, &c., of Cupric Chloride Solutions.** By N. N. TZUCHANOFF (*J. Russ. Chem. Soc.*, 25, 151—152).—The author has investigated the connection between the colour and the electric conductivity of aqueous solutions of cupric chloride of different strengths at constant temperature. In weak solutions of a blue colour, the conductivity increases rapidly with the concentration, but the rate of increase falls off as the solution becomes green. A maximum conductivity is finally reached, the subsequent decrease with increasing concentration being accompanied by a change of tint to yellowish-brown.

J. W.

**Cæsium Cuprichlorides.** By H. L. WELLS and L. C. DUPRE (*Zeit. anorg. Chem.*, 5, 300—303).—Four salts were obtained.  $2\text{CsCl}, \text{CuCl}_2$ ; yellow, rhombic prisms.  $2\text{CsCl}, \text{CuCl}_2 + 2\text{H}_2\text{O}$ ; bluish-green crystals, turning yellow in the air.  $3\text{CsCl}, 2\text{CuCl}_2$ ; brown, triclinic crystals.  $\text{CsCl}, \text{CuCl}_2$ ; hexagonal prisms, red by transmitted, black by reflected, light.

C. F. B.

**Cæsium Cuprochlorides.** By H. L. WELLS (*Zeit. anorg. Chem.*, 5, 306—308).—These were prepared by boiling a solution of cæsium and cupric chlorides in hydrochloric acid with copper wire, and then allowing the solution to crystallise.  $\text{CsCl}, 2\text{CuCl}$  and  $3\text{CsCl}, 2\text{CuCl}$ ; colourless crystals, turning yellowish when dried.  $3\text{CsCl}, \text{CuCl} + \text{H}_2\text{O}$ ; prismatic crystals, very pale yellow in colour.

C. F. B.

**Cæsium Cupribromides.** By H. L. WELLS and P. T. WALDEN (*Zeit. anorg. Chem.*, 5, 304—305).—Two salts were obtained.  $2\text{CsBr}, \text{CuBr}_2$ ; black, rhombic crystals with a greenish shade.  $\text{CsBr}, \text{CuBr}_2$ ; black, hexagonal crystals with a shade of bronze; crystallisation from water converts these into the first-mentioned salt.

C. F. B.

**Oxides contained in Cerite, Samarskite, Gadolinite, and Fergusonite.** By W. GIBBS (*Amer. Chem. J.*, 15, 546—566).—A description is given of various attempts that were made in order to separate the oxides contained in certain specimens of gadolinite, samarskite, and fergusonite. The methods employed were those of fractional precipitation or crystallisation, the salts used being the oxalates, oxychlorides, the double salts with sodium sulphate, and with the various cobaltamine sulphates, the lactates, and the double

salts with mercurous nitrate *plus* mercuric oxide, with acid molybdates, and with phosphotungstates and phosphomolybdates. The methods were often only imperfectly worked out, and the whole paper is somewhat disconnected, and cannot be satisfactorily abstracted.

As a means of determining the "mean atomic mass" of a fraction, it is recommended to precipitate with oxalic acid, carefully mix the dried oxalates in a mortar, and convert a weighed portion by ignition into oxides.

C. F. B.

**Chemical Behaviour of Glass.** By F. FOERSTER (*Ber.*, 26, 2915—2922).—In continuation of his previous work on the action of water and of aqueous alkali and salt solutions on glass (*Abstr.*, 1892, 1401), the author has now investigated the behaviour of acids towards glass. Round flasks of various kinds were employed, the glass, unless otherwise stated, being a calcium-alkali glass, such as is usually applied to chemical purposes; the acid was allowed to act for six hours at 100°. With the same kind of glass, the action, which is always less than that of pure water, is independent both of the nature of the acid and also of its concentration between the limits N/1000 and 10N. With concentrated acids at 160—190°, the nature of the acid is without effect, whilst the amount of change decreases with increasing concentration. The same result was obtained with hydrochloric acid at 260—270°. Emmerling's results, which led him to the contrary conclusion, are probably incorrect. Acids appear, therefore, to be indifferent towards glass; the action which actually takes place is due simply to the water which is always present, and which dissolves alkali; this rapidly attacks the glass, but the stronger the acid the more quickly will the alkali be neutralised. This view receives additional support from the fact that, in comparison with water, acids dissolve larger quantities of alkali and less silica from the glass.

The difference in behaviour towards concentrated acids between glass and other calcium-alkali silicates is noteworthy; the compound  $\text{Na}_2\text{O}, \text{SiO}_2$  is more readily decomposed by concentrated than by dilute acids, whilst sodium silicate with the composition  $\text{Na}_2\text{O}, 3\text{SiO}_2$  behaves like glass in this respect. The reaction is conditioned both by the nature of the bases, and by the relative proportion of silica present; this is shown from the fact that, towards acids, lead crystal glass behaves like calcium-alkali glass, but their action on flint glass, which is poorer in silica, increases with the concentration and differs according to the nature of the acid. Jena thermometer glass 16<sup>III</sup>, which contains zinc, calcium and sodium, is more rapidly acted on by concentrated than by dilute hydrochloric acid at 190°, whilst a calcium-sodium glass of equivalent composition behaves in the usual manner. Pure sulphuric acid attacks calcium-alkali glass less rapidly than pure water at 100°; the action slowly increases with rising temperature; the vapour acts comparatively vigorously, and the glass becomes covered with a network of alkali sulphate crystals.

Carbonic anhydride resembles acids in its action; the "weathering" of glass is chiefly caused by the action of moisture. Glass of every kind combines chemically with more or less water, a graduated series

of compounds being obtained, which form connecting links between fresh glass and the substances that are found in solution. The paper concludes with tables showing (1) the composition of the six better kinds of glass employed for chemical purposes; (2) their relative stability towards water, alkalis, and alkaline carbonates. The best glass mentioned has the following composition:— $K_2O = 6.2$ ;  $Na_2O = 6.4$ ;  $CaO = 10.0$ ;  $MnO = 0.2$ ;  $Al_2O_3 + Fe_2O_3 = 0.4$ ;  $SiO_2 = 76.8$  per cent.; the ratio  $R_2O : RO : SiO_2 = 0.95 : 1.716$ ; it contains 10.4 mols. of alkali in 100 mols., and is, therefore, almost identical with the glass used by Stas in his atomic weight determinations.

J. B. T.

**Manganese.** By O. PRELINGER (*Monatsh.*, 14, 353—370).—Manganese amalgam is prepared by passing an electric current (11 volts; 22—23 c.c. electrolytic gas per minute) from a cathode of pure mercury (20 c.c.) through a saturated aqueous solution of pure manganous chloride (75 c.c.) to an anode of carbon or platinum-iridium contained in a porous vessel. The temperature rises to  $70^\circ$ , and after 5—6 hours the mercury assumes a pasty consistence. The paste is quickly washed in running water without undergoing appreciable decomposition, the excess of mercury squeezed out through linen, and the residue dried over calcium chloride in an atmosphere of hydrogen.

The solid amalgam thus obtained is broken into small pieces and subjected to great pressure (2000 kilos. per sq. cm.) for several hours. The peripheral portion of the pressed cake is broken off, and the central portion broken up and again compressed. The operation is repeated until samples punched from the centres of successive discs yield constant analytical results. Analyses of three distinct preparations yielded practically identical results, pointing to the composition  $Mn_2Hg_6$ . It corresponds with the cadmium compound  $Cd_2Hg_6$ .

*Manganese-mercury*,  $Mn_2Hg_6$ , has a slate-grey colour, and assumes a metallic lustre when rubbed or cut. At ordinary temperatures, it oxidises very slowly in the air, metallic mercury being eliminated. At  $100$ — $110^\circ$ , it decomposes slowly into its elements. It decomposes water and acids at the ordinary temperatures. The sp. gr. is 12.828, a number greater than that, 12.532, calculated from the sp. gr. of its constituents, so that contraction takes place in the formation of the compound. Manganese-mercury is electro-positive to manganese, so that heat is probably absorbed in its formation. A solution of the compound in mercury is not attacked by dry air, but is quickly oxidised by moist air to manganic oxide,  $Mn_2O_3$ , which forms a fine dust on the surface of the liquid.

When manganese-mercury is gently ignited in a stream of pure dry hydrogen (free from oxygen), pure manganese remains behind, uncontaminated with mercury or hydrogen. The *manganese* forms a grey, porous mass, which may be ground into a slate-coloured powder, perfectly stable in air. If the temperature does not reach dull redness in the ignition, however, the metal is set free in a pulverulent spontaneously-inflammable form. The metal cannot be made to exhibit lustre. The sp. gr. of the powdered metal is 7.4212 and the atomic volume (at. wt. = 54.8) 7.385. Manganese powder is

neither magnetic nor magnetisable at ordinary temperatures. It attacks water, slowly in the cold, rapidly when heated. It has little action on concentrated sulphuric acid in the cold, but attacks it rapidly on heating gently, sulphurous anhydride being formed. It liberates hydrogen from dilute sulphuric acid. The action on concentrated nitric acid is explosively violent. It displaces hydrogen from hydrochloric and acetic acids and sodium hydroxide. From aqueous ammonium chloride it liberates ammonia and hydrogen. It reduces metals with great rapidity from warm solutions of their salts (preferably sulphates); the excess of manganese may be dissolved by ammonium chloride. Arsenic, antimony, copper, lead, bismuth, tin, iron, nickel, cobalt, chromium, cadmium, and zinc are thus reduced. The reduction of the magnetic metals may be conveniently demonstrated by means of a compass needle, the latter being deflected after, although not before, the addition of the manganese. JN. W.

**Iron Nitride.** By G. J. FOWLER (*Chem. News*, 68, 152—153).—By exposing iron, reduced from the hydroxide by hydrogen, to a fairly rapid current of ammonia, at a temperature slightly above the melting point of lead, until its weight becomes constant, iron nitride,  $\text{Fe}_2\text{N}$ , is obtained as a feebly magnetic, grey powder. It dissolves in hydrochloric acid, yielding ferrous chloride, ammonium chloride, and hydrogen; it burns in chlorine to ferric chloride and nitrogen; ammonia or ammonium salts are produced when it is heated in hydrogen at the temperature of its formation; in steam at  $100^\circ$ , or in hydrogen sulphide at  $200^\circ$ , or by treatment with hydrogen peroxide and sulphuric acid. By simply heating, it is resolved into iron and nitrogen, but remains unchanged in nitrogen at  $440^\circ$ , or when heated in carbonic oxide or with phenol at  $200^\circ$ ; with ethylic iodide, however, in a sealed tube at  $200^\circ$ , ferrous iodide, ammonium iodide, ethylene, and hydrogen are formed. Its heat of formation is about 3 cal. These results agree with many of Stahlschmidt's observations (*Ann. Phys. Chem.*, 125, 37). D. A. L.

**Constitution of Cobalt, Chromium, and Rhodium Bases.** By S. M. JÖRGENSEN (*Zeit. anorg. Chem.*, 5, 147—196; compare Abstr., 1892, 782, 783).—The first part of this paper deals with the views put forward by A. Werner concerning the structure of ammonio-metallic salts (Abstr., 1893, ii, 379); the author does not regard them as being at variance with the views promulgated by himself and Blomstrand.

The author next describes the best method of preparing the croceocobalt salts from xanthocobalt chloride, and a series of salts, which he terms flavocobalt salts, isomeric with the croceocobalt salts.

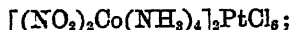
Flavocobalt nitrate,  $(\text{NO}_2)_2\text{Co}(\text{NH}_3)_4\text{NO}_3$ , is prepared by dissolving carbonatotetraminecobalt nitrate (*Zeit. anorg. Chem.*, 2, 282) in cold dilute nitric acid, and adding crystallised sodium nitrite. After being warmed for a few minutes on the water bath, the liquid is cooled, and dilute nitric acid is added. A mixture of the acid and normal salts crystallises, and may be converted entirely into

the normal salt by washing with 95 per cent. alcohol. The flavocobalt nitrate dissolves in 33 parts of cold water, whilst the croceocobalt nitrate requires 400 parts of cold water for its solution.

A detailed comparison of the reactions of croceo- and flavo-cobalt nitrates follows, and the *dinitrate*,  $(\text{NO}_2)_2\text{Co}(\text{NH}_3)_4\text{NO}_3\cdot\text{HNO}_3$ ; the *sulphate*,  $[(\text{NO}_2)_2\text{Co}(\text{NH}_3)_4]_2\text{SO}_4$ ; the *chromate*,



the *dichromate*,  $[(\text{NO}_2)_2\text{Co}(\text{NH}_3)_4]_2\text{Cr}_2\text{O}_7$ ; the *platinosochloride*,  $[(\text{NO}_2)_2\text{Co}(\text{NH}_3)_4]_2\text{PtCl}_4$ ; the *platinochloride*,



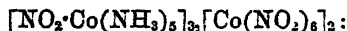
and the *aurochloride*,  $(\text{NO}_2)_2\text{Co}(\text{NH}_3)_4\text{AuCl}_4$ , are described. To prepare the xanthocobalt salts, chloropurpureocobalt chloride is warmed with water and ammonia; the liquid is filtered from some precipitated cobalt oxide, cooled, and neutralised with dilute hydrochloric acid; sodium nitrite and hydrochloric acid are next added, whereon a red precipitate is thrown down. This is an isomeride of xanthocobalt chloride, and is provisionally named *nitritocobalt chloride*; it is readily converted into the xantho-salt by dissolving it in water containing a few drops of ammonia, and adding strong hydrochloric acid, which throws down the xanthochloride.

The reactions of the xantho-salts are detailed, and the *sulphates*,  $4[(\text{NO}_2)_2\text{Co}(\text{NH}_3)_5\text{SO}_4]\cdot 3\text{H}_2\text{SO}_4$  and  $\text{NO}_2\cdot\text{Co}(\text{NH}_3)_5\text{SO}_4$ , are described.

Xanthocobalt chloride dissolves in 50 parts of cold water; nitritocobalt chloride dissolves in 200 parts. Differences between the reactions of the two salts are described, and it is shown that the nitrito-salt is not a roseo-salt.

The author has prepared a *luteorhodium rhodium chloride*,  $\text{Rh}(\text{NH}_3)_4\text{Cl}_3\cdot\text{RhCl}_3$ , and a *chloropurpureorhodium rhodium chloride*,  $3\text{RhCl}(\text{NH}_3)_5\text{Cl}_3\cdot 2\text{RhCl}_3$ .

The following salts are described:—*Luteocobalt cobaltinitrite*,  $\text{Co}(\text{NH}_3)_4\text{Co}(\text{NO}_2)_6$ ; *xanthocobalt cobaltinitrite*,



*croceocobalt cobaltinitrite*,  $[(\text{NO}_2)_2\text{Co}(\text{NH}_3)_4]_3\text{Co}(\text{NO}_2)_6$ ; *flavocobalt cobaltinitrite*,  $[(\text{NO}_2)_2\text{Co}(\text{NH}_3)_4]_3\text{Co}(\text{NO}_2)_6$ ; *luteocobalt diaminecobaltinitrite*,  $\text{Co}(\text{NH}_3)_4[(\text{NO}_2)_2(\text{NH}_3)_2\text{Co}(\text{NO}_2)_2]_3$ ; *xanthocobalt diaminecobalt nitrite*,  $\text{NO}_2\cdot\text{Co}(\text{NH}_3)_5[(\text{NO}_2)_2(\text{NH}_3)_2\text{Co}(\text{NO}_2)_2]_3$ ; *croceocobalt diaminecobalt nitrite*,  $(\text{NO}_2)_2\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2\text{NH}_3\cdot\text{Co}(\text{NO}_2)_2$ ; *flavocobalt diaminecobalt nitrite*,  $(\text{NO}_2)_2\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2(\text{NH}_3)_2\text{Co}(\text{NO}_2)_2$ ; *triaminecobalt nitrate*,  $\text{Co}(\text{NH}_3)_3(\text{NO}_3)_3\cdot 3\text{H}_2\text{O}$ ; *dichrocobalt chloride*,  $\text{Co}(\text{NH}_3)_3(\text{OH})_2\text{Cl}_3$ ; *nitrotriaminecobalt nitrite*,  $\text{NO}_2\cdot\text{Co}(\text{NH}_3)_3(\text{NO}_2)_2$ ; and *chloronitrotetraminecobalt chloride*,  $(\text{NO}_2)\text{ClCo}(\text{NH}_3)_4\text{Cl}$ .

A. G. B.

**Atomic Weight of Molybdenum.** By E. F. SMITH and P. MAAS (*Zeit. anorg. Chem.*, 5, 280—282).—Pure sodium molybdate was heated in a current of hydrochloric acid: the reaction  $\text{Na}_2\text{MoO}_4 + 4\text{HCl} = 2\text{NaCl} + \text{MoO}_3\cdot 2\text{HCl} + \text{H}_2\text{O}$  took place, and the residue, which consisted of pure sodium chloride, was weighed. The atomic



weight was found to be 96.087 ( $O = 16$ ) as a mean of 10 determinations, which varied from 96.130 to 96.081. C. F. B.

**Tin and Stannic Oxide.** By F. EMICH (*Monatsh.*, 14, 345—352).—When pure block tin is heated in a stream of air or in an open porcelain crucible, drops of molten metal ooze after some hours from beneath the superficial crust of stannic oxide, and, becoming superficially oxidised, gradually assume curious forms resembling bulbs and worms. After 12 hours' heating, the oxide is crystalline, and consists of microscopic, needle-like, rhombic plates of sp. gr. 7.01. The crystals seem to be formed directly from the metal, as the amorphous oxide prepared from "metastannic acid" may be heated in contact with tin in an indifferent atmosphere without undergoing change of form. They are not due to the oxidation of metallic vapour, since the metal is not volatile at the temperatures employed.

When tin containing traces of iron (0.05 per cent.) is heated in the manner described above, most of the iron is eliminated with the first portions of stannic oxide, a mere trace (0.001 per cent.) being left in the tin. The stannic oxide assumes a colour varying from brown to yellow with the amount of iron, thus serving as a good qualitative test for that impurity. The oxide formed after the iron has been eliminated is snow-white. Jx. W.

**Thorium Compounds.** By P. JANNASCH, J. LOCKE, and J. LESINSKY (*Zeit. anorg. Chem.*, 5, 283—287).—This is a preliminary paper. It contains a detailed account of the means adopted to obtain pure thorium oxalate from thorite and orangite. From the hydroxide the bromide ( $? ThBr_4 + 10H_2O$ ) and iodide were prepared; they form very deliquescent crystals. C. F. B.

**Double Haloids of Antimony and Rubidium.** By H. L. WHEELER (*Zeit. anorg. Chem.*, 5, 253—263; and *Amer. J. Sci.*, [3], 46, 269—279).—The double haloids enumerated below have been prepared by concentrating solutions in 10 per cent. halogen acids of the two haloids in varying proportions; the proportion by molecules of rubidium to antimony haloid in the solution is given by the numbers in square brackets. The 23 : 10 salts might equally well have a 16 : 7, 9 : 4, or 7 : 3 formula; the 3 : 2 salts are isomeric with the corresponding arsenic compounds.

$RbCl, 2SbCl_3 + H_2O$  [1 : 10, 6, or 8]; colourless, monoclinic plates melting at  $77^\circ$ ,  $a : b : c = 1.699 : 1 : 0.820$ ;  $\beta = 89^\circ 28'$ .

$RbCl, SbCl_3$  [1 : 4 or 3]; colourless, monoclinic crystals,  $a : b : c = 1.732 : 1 : 1.085$ ;  $\beta = 65^\circ 34'$ .

$3RbCl, 2SbCl_3$  [1 : 1 $\frac{1}{2}$ ]; yellow rhombohedra, exhibiting rhombohedral tetartohedry.  $23RbCl, 10SbCl_3$  [1, 4, or 6 : 1]; colourless, hexagonal plates.

$3RbBr, 2SbBr_3$  [2.3 or 5 : 1]; lustrous, yellow, hexagonal plates.  $23RbBr, 10SbBr_3$  [6, 8, or 13 : 1]; lustrous, yellow needles.

$3RbI : 2SbI_3$ , red rhombohedra.

C. F. B.

**Recovery of Osmium from Residues.** By W. GULEWITSCH (*Zeit. anorg. Chem.*, 5, 126—128).—The osmium residues obtained in histological laboratories are the solution of osmium tetroxide drained or filtered from the treated objects, and the *débris* of the objects themselves. The solutions are treated with zinc and hydrochloric acid, the osmium is collected, washed successively with hydrochloric acid, water, alcohol, and ether, and then allowed to dry at a low temperature. The osmium is then transferred to the hind portion of a combustion tube which has a constriction containing an asbestos plug in front of the osmium; the forward portion of the tube is bent into a U, and the end is drawn out to a fine tube which is bent over and placed in a flask; the U-tube and the flask are surrounded by a freezing mixture. A current of dry oxygen is passed through the apparatus, the osmium is gently heated, and the resulting tetroxide condensed in the U bend; if the process be properly conducted, none of the tetroxide will be carried over into the flask.

The osmium cannot be directly sublimed as tetroxide from the objects because of the organic matter which they contain. These residues are warmed in a retort with 10 times their weight of aqua regia, and the resulting solution is distilled until two-thirds have passed over, the receiver being well cooled. The distillate is again distilled until two-thirds have passed over, the second distillate is reduced by zinc, and the precipitated osmium is treated as described above. A large excess of zinc must be used, and the liquid must be warmed, in order that the osmium may be precipitated in a condition in which it will be retained by a filter. A. G. B.

## Mineralogical Chemistry.

**Vanadiniferous Coal.** By A. MOURLOT (*Compt. rend.*, 117, 546—548).—This coal is analogous to that recently described by Kyle from the province of Mendoza, in the Argentine Republic. Its sp. gr. is only 1.15—1.20. It contains ash, 0.63; H, 4.73; N, 1.67; C, 85.03. The composition of the ash is—*Part soluble in acids*:  $V_2O_5$ , 38.5;  $SO_3$ , 12.1;  $P_2O_5$ , 0.8;  $Fe_2O_3$ , 4.1;  $Al_2O_3$ , 4.0;  $CaO$ , 8.44;  $K_2O$ , 1.8. *Part insoluble in acids*:  $SiO_2$ , 13.6;  $Al_2O_3$ , 5.5;  $Fe_2O_3$ , 9.4;  $MgO$ , 0.9.

The percentage of vanadic anhydride in the original coal is 0.24.

C. H. B.

**Nesquehonite.** By C. FRIEDEL (*Zeit. Kryst. Min.*, 22, 279; from *Bull. soc. fran. min.*, 14, 60).—In the anthracite mines at Mure, in Isère, there occurs a fibrous mineral resembling aragonite, which, on exposure to air, becomes of a silky lustre, and has the composition  $MgCO_3 + 3H_2O$ . Analysis yielded

MgO.	H <sub>2</sub> O.	CO <sub>2</sub> .
32.97	38.85	31.85

The mineral has a prismatic cleavage of about  $115^\circ$  parallel to the fibres. It is identical with the nesquehonite of Genth and Penfield.

B. H. B.

**Xenotime from North Carolina.** By W. E. HIDDEN (*Amer. J. Sci.*, [3], 46, 254—257).—A few small crystals of transparent xenotime have been found with monazite at a locality about 1 mile south-east of Sulphur Springs, Alexander Co., North Carolina. The measurements of these new crystals do not vary essentially from those of vom Rath and Klein.

Green xenotime occurs as a rare constituent of the auriferous gravels of the Brindletown gold region of Burke Co., North Carolina. It has not as yet been found *in situ*. Within brown, opaque crystals, the new green variety was found. It appears to represent the original condition, whilst the brown variety is an alteration product. The new material is of a bottle-green colour and transparent, and when finely pulverised is soluble in hot hydrochloric acid. The author gives the results of analyses of both the green and the brown variety. A very complex mixture is shown. It seems probable that xenotime is either a silico-phosphate, like some monazite and anerlite, or it is often mechanically mixed with some cyrtolite and other silicates of the rare earths.

B. H. B.

**Nephrite from British Columbia.** By B. J. HARRINGTON (*Zeit. Kryst. Min.*, 22, 310—311; from *Trans. R. Soc. Canada*, 1890, 61).—The author communicates the following analyses of nephrite.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO.	MnO.	CaO.	MgO.	Loss.	Total.
I. 55·32	2·42	5·35	0·52	14·00	20·16	2·16		99·93
II. 56·93	0·18	4·59	0·17	12·99	22·38	2·64		99·93
III. 56·54	0·40	3·61	0·16	13·64	22·77	2·92		100·04
IV. 56·96	0·51	3·81	0·53	13·29	22·41	2·91		100·42

I. Rounded mass from an Indian tomb at Lytton, on the Fraser River. Colour, olive-green. Hardness over 6, and very tough. Sp. gr., 3·0278. II. Fragment of an axe from the same locality. Colour, greyish-green. Sp. gr., 3·003. III. A worked fragment of pale green colour from the vicinity of Lytton. It shows small laminae of tremolite. Sp. gr., 3·01. IV. Small fragment from the Lewes River, near the frontier of Alaska. Colour, greyish-green. Sp. gr., 3·007. The author shows that the composition of these nephrites is the same as that of specimens from other parts of the world. Jadeite has not yet been found in British Columbia.

B. H. B.

**Talc from Madagascar.** By E. JANNETTAZ (*Zeit. Kryst. Min.*, 22, 279; from *Bull. soc. fran. min.*, 14, 67).—A fibrous, pale green mass with pearly lustre from Ambohimanga-Atsimo, in Madagascar, proved to be talc. It is probably a pseudomorph. Analysis yielded

H <sub>2</sub> O.	SiO <sub>2</sub> .	FeO.	MgO.
5·1	62·3	2·6	29·4

There have also been found in Madagascar prismatic crystals of

sapphire and zircon, pink tourmaline, and rubellite in nine-sided prisms with rhombohedral termination. B. H. B.

**Topaz in the Fichtelgebirge.** By K. OEBBEKE (*Zeit. Kryst. Min.*, 22, 273—275).—Small, yellowish crystals of topaz were discovered in 1879 by v. Gümbel in the granite of Rudolphstein. The author describes two new occurrences of topaz at the Epprechtstein and the Gregnitzgrund, in the Fichtelgebirge, which support v. Gümbel's view that topaz would probably be found in other granites in that district. B. H. B.

**Canadian Spessartine.** By B. J. HARRINGTON (*Zeit. Kryst. Min.*, 22, 309; from *Canadian Rec. Sci.*).—Garnet occurs in felspar and mica at the Villeneuve Mica Mine at Villeneuve, Quebec. The mine has been opened on a vein of coarse-grained granite consisting of quartz, muscovite, orthoclase, albite, and small quantities of tourmaline and garnet. Uraninite and monazite are also met with. The garnet examined was derived from the mica. The largest crystal had a diameter of about 10 mm., and was bright red. Its sp. gr. is 4.117, and analysis shows it to be a manganese garnet similar in composition to the original spessartine. B. H. B.

**Vesuvian in Ireland.** By J. P. O'REILLY (*Zeit. Kryst. Min.*, 22, 300; from *Proc. R. Irish Acad.*, 1891, 446).—Vesuvian was found as a honey-yellow, lamellar substance in a manganiferous iron ore from the Cambrian strata in Calliagh, Monaghan Co. Analysis gave the following results.

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	MnO	CuO	Na <sub>2</sub> O	Loss.
40.06	16.03	37.46	4.23	1.16	0.21	1.00	2.07

B. H. B.

**Chemical Nature of Axinite.** By H. RHEINECK (*Zeit. Kryst. Min.*, 22, 275—277).—Rammelsberg's investigations led to the formula  $Al_2Si_4BM_3HO_{16}$  for axinite. This, however, is shown by the author to be not in accord with the results of analyses recently published by Whitefield, Genth, and Baumert. Calculations are given showing the composition of axinite from Oisans, Cornwall, Franklin in New Jersey, Guadalucazar in Mexico, and Radauthal in the Hartz. B. H. B.

**Minerals from the Manganese Mines of St. Marcel, Italy.** By S. L. PENFIELD (*Amer. J. Sci.*, [3], 46, 283—295).—*Alurgite*.—In 1865, Breithaupt described, under this name, a deep red mica from St. Marcel, in Piedmont, Italy. Since then it has never been investigated. Further examination, however, shows that it is a distinct species. The crystallisation is monoclinic, and the structure micaceous. The colour is a characteristic, deep, brownish copper-red. The hardness is 3, and the sp. gr. 2.84. Analysis yielded

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Mn <sub>2</sub> O <sub>3</sub>	MnO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	H <sub>2</sub> O	Total.
53.22	21.19	1.22	0.87	0.18	6.02	11.20	0.34	5.75	99.99

Chemically, this mica is distinct from any known species. It is more closely related to lepidolite than to any of the others.

**Jadeite.**—The alurgite is embedded in a pyroxene rich in soda, resembling in structure a rather coarsely crystallised jadeite, and agreeing in composition with a jadeite from Mexico, analysed by Damour (*Abstr.*, 1883, 1066).

**Violan.**—This name was given, in 1833, by Breithaupt to a rare blue mineral found at Piedmont. Published analyses of this mineral show considerable variation. The results of the author's analysis show that the mineral is essentially a blue variety of diopside, containing small quantities of various well-recognised pyroxene molecules. The composition may be expressed as a mixture of the following metasilicates.

MgCa(SiO <sub>3</sub> ) <sub>2</sub> , diopside .....	90·8 per cent.
NaAl(SiO <sub>3</sub> ) <sub>2</sub> , jadeite .....	4·1 „
NaFe(SiO <sub>3</sub> ) <sub>2</sub> , acmite .....	2·4 „
NaMn(SiO <sub>3</sub> ) <sub>2</sub> ? .....	2·7 „

B. H. B.

**Monticellite Crystals obtained in Lead Smelting.** By W. v. GÜMBEL (*Zeit. Kryst. Min.*, 22, 269—270).—At Freihung, in the Upper Palatinate, lead ores occur in sandstone in such quantity that at one time the mining industry was of considerable importance. Owing to lack of pumping machinery, the mines were, however, abandoned in the middle of the present century. On reopening the mines recently, interesting specimens of galena and cerussite have been met with. The ore is smelted in a Pilz furnace. The silicate slags formed, on slow cooling, crystallise out as well-developed acicular crystals, giving, on analysis, the following results.

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MnO	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>
33·04	1·10	7·91	31·53	1·16	23·52	1·18	0·58	0·24	0·31

The sp. gr. was found to be 3·58, and the crystals were isomorphous with those of the members of the olivine group, the form observed being 2P<sub>∞</sub>, ∞P, ∞P<sub>∞</sub>. This crystallised slag is thus a monticellite, in which the magnesia is replaced by ferrous oxide.

B. H. B.

**Serpentine from Bray Head.** By J. P. O'REILLY (*Zeit. Kryst. Min.*, 22, 300; from *Proc. R. Irish Acad.*, 1891, 503).—An intrusive rock of Cambrian age, at Bray Head, Dublin, was formerly described as greenstone. The author shows that it is really a serpentine, probably formed by the alteration of a diabase porphyry.

B. H. B.

**New Meteorite from Hamblen Co., Tennessee.** By L. G. EAKINS (*Amer. J. Sci.*, [3], 46, 283—285).—This meteorite was found in September, 1887, on a ridge 6 miles from Morristown, Tennessee. The various pieces found weigh about 36 lbs.; most of them exhibit much surface oxidation, a fresh fracture showing a grey colour, with numerous metallic particles of nickel-iron. The latter gave the following results on analysis.

Fe.	Ni.	Co.	Cu.	P.	S.	Total.
90·92	7·71	0·80	trace	0·19	0·04	99·66

The siliceous portion of the meteorite gave the following results.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Cr <sub>2</sub> O <sub>3</sub> .	FeO.	NiO.	MnO.	CaO.	MgO.
I.	16.79	8.33	—	4.88	0.39	—	5.19	1.34
II.	31.47	9.25	0.82	6.55	—	0.47	2.24	11.16
	K <sub>2</sub> O.	Na <sub>2</sub> O.	P <sub>2</sub> O <sub>5</sub> .	S.	Total.			
I.	—	—	0.46	0.25	37.63			
II.	0.02	0.12	—	—	62.10			

I, portion soluble in hydrochloric acid; II, insoluble portion. In many stony meteorites, olivine forms the bulk of the soluble portion. In this case, analysis shows olivine to be present in but small proportion, if at all.  
B. H. B.

## Physiological Chemistry.

**Respiratory Exchange in Shivering.** By C. RICHET (*Compt. rend. Soc. Biol.*, 1893, 33—35).—Shivering is regarded as an act to produce more heat when the blood has been cooled. The experiments were tried on chloralised dogs, in which there is great lowering of the amount of carbonic anhydride produced. On shivering, this rises, especially if the shivering is violent, and the respiratory quotient rises also.  
W. D. H.

**Proteid-poor Nutrition.** By T. ROSENHEIM (*Pflüger's Archiv*, 54, 61—71).—A number of experiments on dogs are recorded in which a diet poor in nitrogen was given. The analyses of the food and excreta, and the daily weight of the animal, are given in tables. These experiments confirm the previous observations of the author, that such diets are very harmful; the animal becomes ill and apathetic, similar to the condition observed in starvation. *Post-mortem* examination showed extensive fatty degeneration, especially of the liver and alimentary tract.  
W. D. H.

**Influence of Muscular Work on the Excretion of Sulphur.** By C. BECK and H. BENEDICT (*Pflüger's Archiv*, 54, 27—61).—During muscular work the excretion of sulphur is increased. This is followed (when the work has ceased) by a corresponding diminution. The increase falls especially on the oxidised sulphur; the non-oxidised sulphur due to proteid metabolism may be lessened. The relationship of these two forms of sulphur is recommended as an indication of the disintegration of proteid in the body.  
W. D. H.

**Circulating Proteid.** By E. PFLÜGER (*Pflüger's Archiv*, 54, 333—419).—This is a long, critical, and polemical article directed against Voit's theory of the distinction between organ proteid and circulating proteid. The tendency of the article is to show that

metabolic processes in proteid matter occur in the cells, that is, in organised proteid; but it is admitted that in the organised cell substance there are different kinds of organised proteid molecules, different degrees of organisation. W. D. H.

**How does Proteid Nutrition influence Proteid Metabolism in Animal Cells?** By B. SCHÖNDORFF (*Pflüger's Archiv*, 54, 420—483).—The increase of urea in the blood after proteid food is not due to a diffusion of urea from the tissues into the blood, but to a real new formation of urea in the liver from the nitrogenous decomposition products of cellular activity.

By leading the blood of a starving animal through the organs and liver of a well-nourished one, the amount of urea in the blood is increased. By leading the blood of a starving animal through the organs and liver of a starving animal, there is no change in the amount of urea. By leading the blood of a well-nourished animal through the organs and liver of a starving animal, the amount of urea in the blood is diminished.

Therefore, the amount of proteid decomposition depends on the nutritive condition of the cells, and not on the proteid contents of the "intermediate lymph stream." The amount of urea in the blood depends on the condition of the animal, falling during hunger (minimum 0.0348 per cent.), and rising to a maximum during the time of greatest urea formation (0.153 per cent.). The decomposition products from which the liver forms urea are probably ammonium salts. W. D. H.

**Sulphur in Human and Animal Tissues.** By H. SCHULZ (*Pflüger's Archiv*, 54, 555—573).—In the dried organs of a man, aged 39, the percentage of sulphur was found to vary from 0.57 in the brain to 1.03 in the jejunum. In the muscles of various animals, the percentage varied from 0.86 to 1.33; in the human aorta, from 0.45 to 0.67; and in the human vena cava, from 0.28 to 0.73.

W. D. H.

**Non-coagulable Blood.** By C. J. MARTIN (*J. Physiol.*, 15, 375—379).—When nucleo-albumins (Wooldridge's tissue fibrinogens) are introduced into the circulation, a state of non-coagulability is sometimes produced. This is considered by Wright and Pekelharung to be due to the cleavage of the nucleo-albumin into nuclein and a peptone-like substance, to the latter of which the non-coagulability of the blood is due. This view has been already questioned by Halliburton and Brodie (*Brit. Med. J.*, ii, 1893, 631), and the present paper shows conclusively that no peptone or proteose is present in the blood in the condition in question.

The method adopted is to mix the blood with an equal volume of 10 per cent. trichloroacetic acid. This is raised to the boiling point, and filtered hot. The filtrate gave no indications of the presence of either proteose or peptone. This method, a modification of Starling's, is well calculated to detect these substances, as control specimens of blood to which peptone or proteose was added showed. The

object of boiling and keeping the mixture hot during filtration is that the proteoses are partly precipitable by the acid in the cold, but this precipitate dissolves on heating. W. D. H.

**Results of feeding Cows at Grass on Meal.** By J. P. ROBERTS and H. H. WING (*Bied. Centr.*, 22, 728—732).—Eight cows were pastured only, whilst another eight received mixed meals in addition to the pasturage. It was found that whilst the eight cows receiving meals gave a larger daily yield of milk, yet the percentage of fat in the milk was lower than that found in the milk from cows fed on grass only; at the same time, the excess of milk thus obtained paid for the extra food given. E. W. P.

**Mule's Milk.** By A. B. AUBERT and D. W. COLBY (*Chem. News*, 68, 168—169).—Two samples of a mule's milk were examined, one collected about six weeks, the other about nine weeks, after the flow of milk had commenced; the mule was 11 years old, in work, fed on oats and hay, and yielded about 2 quarts of milk daily, being milked at frequent intervals. The milk was pure white, alkaline; turning sour, after long standing, with the separation of a fine, floating, flocculent coagulum instead of a curd; the fat globules were very small; the casein is not readily precipitated by dilute acetic acid or by carbonic anhydride; this was especially the case with the first sample. The analytical numbers given are

Sp. gr. at 15° .....	1.032	1.033
Total solids.....	10.65	10.86
Proteids.....	2.94	2.31
Fat.....	1.86	1.98
Sugar.....	—	6.03
Ash.....	—	0.53

D. A. L.

**Secretion of Urine.** By L. LIEBERMANN (*Pflüger's Archiv*, 54, 585—606).—In a previous paper (*Abstr.*, 1893, ii, 27), an acid constituent of the kidney substance, named lecithalbumin, is described. The properties of lecithalbumin generally are discussed in *Pflüger's Archiv*, 54, 573—585. This material is obtained from the tissue as a residue after artificial gastric digestion. It is like nuclein; it is believed to come from the nucleus, and it possesses the power of interacting with a basic phosphate,  $\text{Na}_2\text{HPO}_4$ , yielding an acid filtrate. Similar substances are obtained from blood serum or from defibrinated blood. The reaction of the fresh kidney is not constant; it is usually neutral; it may be alkaline or slightly acid; *post mortem*, it invariably soon becomes acid. This inconstancy indicates that the reaction of the kidney is a variable factor during life, and is probably related to the stages of its secretion. The acidity of the kidney is believed to be due to the lecithalbumin, which is stated to be the most abundant constituent of the cell substance. This is confirmed by microchemical staining; the nucleus, and to a less extent the cell protoplasm, taking up basic dyes.

It is further advanced that the acidity of the urine is due to the



interaction of sodium urate and disodium hydrogen phosphate; these are contained in the blood plasma, and their interaction is brought about by the acid constituent of the cells (lecithalbumin) which the secretion on its way from blood to urinary tubules must necessarily come in contact with.

W. D. H.

**Fermentation and Carbohydrates in Urine.** By E. SALKOWSKI (*Pflüger's Archiv*, 54, 607—614).—Polemical. An answer to E. Baumann.

**Variations of Glycogenia in Anthrax.** By H. ROGER (*Compt. rend.*, 117, 488—490).—When the anthrax bacillus is cultivated in milky decoctions of liver, all the glycogen is somewhat rapidly destroyed, and the liquid likewise contains no sugar. Now, glycogen is never found in the liver of animals that die of anthrax, but sugar can easily be detected in the liver and the blood.

In the early stages of anthrax, before the bacilli have appeared in the blood, the liver contains large quantities of glycogen, but in later stages, when the blood has become charged with bacilli, all the glycogen has disappeared from the liver. It would seem that as soon as the temperature reaches 39.5° the glycogen disappears, but if the temperature falls to 38°, glycogen appears again in the liver.

In most cases, however, the disappearance of the glycogen coincides with the reduction of the central temperature and the appearance of numerous bacilli in the blood. The disappearance of the glycogen is always accompanied by marked hyperglycæmia. It follows that in anthrax the glycogen is rapidly converted into glucose, and the tissues then become incapable of consuming the sugar furnished by the liver.

The bacilli destroy sugar in liquid cultivations, but seem to be without the power of attacking it in the animal organism.

C. H. B.

**Toxicity and Therapeutic Use of Sodium Fluoride.** By BLAIZOT (*Compt. rend. Soc. Biol.*, 1893, 316—319).—Sodium fluoride has antiseptic properties, a statement of Arthus and Huber which is confirmed in the present paper by further experiments. It is recommended as a lotion in various affections of the skin and mucous membranes; its toxicity is small, 8 centigrams per kilo. of body weight having in rabbits to be injected intravenously to produce poisonous symptoms; the symptoms are slight fever, salivation, and dyspnœa. The animal recovers in a few hours. After a dose of 1 decigram, however, the symptoms are more intense, and the animal dies in a comatose condition.

W. D. H.

**Physiological Action of Apocodeïne.** By L. GUINARD (*Compt. rend. Soc. Biol.*, 1893, 586—590).—The experiments were carried out on dogs, and apocodeïne hydrochloride was injected hypodermically.

The heart is at first accelerated for a short period; the animal then becomes somnolent or sleeps, and the rate of the heart falls. This is entirely of central origin, and the course of the nervous impulses to the heart is by the pneumogastric nerves; the phenomena can be

prevented by section of these nerves. The blood pressure rises in the first and sinks in the second phase; the lowering of pressure is not, however, very great (not nearly as great as that produced by morphine), and is a result of the heart's slower action rather than of vaso-dilatation.

The rate of respiration runs parallel to that of the heart. The body temperature is lowered during the somnolent stage. The quantity of oxygen consumed and carbonic anhydride expired is also considerably lessened. The repose of the skeletal muscles and the slowing of the heart and respiration will partly explain these results; but another factor is believed to be a lessening of inter-organic combustions.

W. D. H.

**Effects of Snake Venom.** By C. J. MARTIN (*J. Physiol.*, 15, 380—400).—The venom investigated was that of the Australian black snake (*Pseudechis porphyriacus*). The poisonous constituents are primary proteoses. The effect on the blood is principally dealt with in the pre-ent communication. The effect resembles that produced by injection of nucleo-albumin, sometimes producing intravascular coagulation, and sometimes, with larger doses, a condition of non-coagulability. On shed blood, a solution of the venom retards coagulation. The venom itself contains no nucleo-albumin. It probably acts by liberating nucleo albumin from the blood corpuscles. This view is supported by observations that show that the venom dissolves both kinds of blood corpuscles to some extent. The very minute doses necessary bear in the same direction.

W. D. H.

## Chemistry of Vegetable Physiology and Agriculture.

**Effect of Calcium Sulphite on Alcoholic Fermentation.** By T. CHIAROMONTE (*Staz. Sper. Agrar.*, 23, 360—379).—The hot climate of the south of Italy makes it difficult to obtain wines which will keep, the high temperature rendering a regular fermentation impossible. After enumerating the various proposed methods for keeping down the temperature of the must during fermentation, the author describes experiments on the action of calcium sulphite, which was shown by Czeppel to lower the temperature of fermenting liquids. Comparative experiments were made, both in a cellar and with smaller quantities in the laboratory, in which one quantity of must had no calcium sulphite added, and others were mixed with different amounts of the salt. The temperature was observed twice daily, and the amounts of alcohol produced each day ascertained. Sp. gr., total acid, and dry matter were also determined.

The following conclusions are drawn from the experimental results:—An addition of 5 to 10 grams of calcium sulphite per hectolitre does not lower the temperature of the fermenting liquid, but rather tends to stimulate the fermentation. A larger amount of sulphite

(20 to 30 grams) retards fermentation, whilst 100 grams per hectolitre stops it altogether. Biernaki has shown (*Arch. Physiol.*, 49, 112) that many substances, mercuric chloride, copper sulphate, potassium permanganate, &c., when added in small quantities, accelerate fermentation (compare also Richet, *Compt. rend.*, 114, 1494).

The stimulating action of calcium sulphite is greater, the larger the amount of ferment. It diminishes the acidity of the wine in proportion to the amount employed, owing to the liberation of the base.

The lime liberated from the sulphite neutralises more or less of the acid of the wine, and thus diminishes the already too low acidity of the southern wines; this can, however, be overcome by adding tartaric acid with the sulphite. Whilst the addition of calcium sulphite in sufficient amount to lower the temperature quite alters the character of the wine, smaller amounts induce more complete fermentation, but the advantage is too slight to make it worth while to employ the salt.

N. H. M.

**Action of Alcohol and Sulphur on Yeast.** By J. DE REY-PAILHADE (*Compt. rend. Soc. biol.*, 1893, 46—47).—Yeast was suspended in its own weight of water, and also in its own weight of alcohol, and the two were compared together. It was found that the alcohol killed the yeast and produced certain substances from the cells which have the power of decolorising (hydrogenising) indigo-carmin and litmus. It is, however, possible to produce the latter result without killing the organisms; this is accomplished by adding to the suspended yeast its own weight of sulphur; this leads to the evolution of hydrogen sulphide, which is then decomposed by the indigo-carmin.

W. D. H.

**Beer Yeast.** By J. EFFRONT (*Compt. rend.*, 117, 559—561).—Experiments made with *Saccharomyces cerevisiae* (*Pastorianus* 1, *Carlsberg*, and *Burton*), show that when yeast is cultivated in a sterilised malt wort containing 200—300 milligrams of alkali fluorides per litre, the power of propagation is reduced to an extent depending on the nature of the yeast. Worts of this kind can, however, serve for the cultivation of all varieties of beer yeast, provided that the latter have been habituated to the presence of fluorides by successive cultivations in solutions containing increasing quantities of fluorides.

The yeasts which have been cultivated in these liquids have a fermenting power very much greater than that of ordinary yeast. After five or six cultivations, this power may be increased as much as 10 times. Further, unlike ordinary yeasts, they can be employed successfully in distilleries without having first been passed through an acid leaven.

C. H. B.

**Transformation of Starch into Sugar by the *Bacillus anthracis*.** By MAUMUS (*Compt. rend. Soc. biol.*, 1893, 107—109).—The *Bacillus anthracis* was grown on potato. The surface of the potato then gave with iodine, not the blue of starch, but the red of dextrin. Other slices were then placed in sterilised water in flasks;

after two to six days at 37°, the liquid gave reduction with Fehling's solution. Later, however (six to seven days), all the sugar had disappeared, having possibly been used as a nutriment for the micro-organisms.

W. D. H.

**Influence of Metallic Salts on Lactic Fermentation.** By A. CHASSEVANT and C. RICHET (*Compt. rend.*, 117, 673—675).—The authors have determined the quantities of various metallic salts required to prevent the lactic fermentation of whey, a distinction being made between the quantity required to arrest reproduction and that necessary to stop fermentation, the former being called the *antigenetic dose* and the latter the *antibiotic dose*. The antigenetic dose varies from 0.5 gram molecule per litre, in the case of magnesium, to 0.000065 in the case of cobalt, the corresponding values for the antibiotic dose being 1.5 and 0.000065 respectively. The order of toxicity of the metals investigated is magnesium, lithium, calcium, strontium, barium, aluminium, manganese, iron, lead, zinc, copper, cadmium, platinum, mercury, nickel, gold, cobalt. In the case of magnesium and platinum, the antibiotic dose is three times as great as the antigenetic dose; in the case of mercury and cobalt, the two doses are identical; in other cases, the ratio varies from 2.5 to 1.2.

C. H. B.

**Proteolytic Action of Bromelin.** By R. H. CHITTENDEN (*J. Physiol.*, 15, 249—310).—Bromelin, the ferment of pine-apple juice, appears to be associated with a peculiar proteose-like substance. In the present paper, attention is paid to the character of the isolated ferment and its action on the three typical proteids, fibrin, egg-albumin, and myosin. The resulting products (proteoses and peptones) were analysed, and full details are given of their properties and percentage composition.

W. D. H.

**Presence of Vegetable Trypsin in Fruit of *Cucumis utilis-simus*.** By J. R. GREEN (*Ann. Agron.*, 19, 508—509).—Ferments which dissolve coagulated albumin are rare in the vegetable kingdom. To the few authentic cases (the pepsic ferment of the fruit of *Carica Papaya*, the papain of Würtz and of Vulpian, and the latex of the common fig tree) the author has added a pepsic ferment found in germinating lupin seeds, and now calls attention to one found in the fruit of *Cucumis utilis-simus*, Roxb., a plant indigenous in India. The juice of this fruit dissolves boiled white of egg; the boiled juice has no such power. It does not depend on microbes, since the addition of thymol does not prevent the action. Salt water dissolves out more of the ferment than pure water. The author believes the ferment to belong to the globulins or allied bodies. Like papain, it resembles trypsin rather than pepsin, and is more active in presence of bases than in neutral or acid media; the products of its action on coagulated albumin are first peptone, afterwards leucine.

J. M. H. M.

**Presence in Fungi of a Ferment analogous to Emulsin.** By E. BOURQUELOT (*Compt. rend.*, 117, 383—386).—23 species of fungi parasitic on living trees, or growing upon dead wood, contain a

soluble ferment, which has the power of decomposing glucosides, such as amygdalin, salicin, and coniferin, and it would seem to be through the medium of this ferment that the fungi are able to utilise as food the various glucosides present in the bark, cambium, and ligneous tissue of the trees or wood on which they live.

No similar ferment could be obtained from nine species of fungi growing upon the soil.

The ferment can be extracted in two ways. The freshly-gathered fungus is placed in an atmosphere saturated with the vapour of ether or chloroform, which causes an abundant exudation of a liquid containing the soluble substances of the cellular fluid. In the other method, the fungus is made into a paste by trituration with sand, and is then extracted with water. C. H. B.

**Formation of Saccharose during the Germination of Barley.** By L. LINDET (*Compt. rend.*, 117, 668—670).—The finely-powdered barley was treated with alcohol of 91°, which dissolves the saccharose with only minute quantities of reducing sugars. After removal of acids by means of lead hydroxide, the rotatory power and reducing power were estimated, before and after inversion, by Clerget's process. 46 hours after the commencement of germination, the percentage of saccharose is 0.99, which, at the end of 70 hours, has increased to 1.05, and at the end of 94 hours to 2.20, and then very slowly increases until it becomes 3.09 at the end of 234 hours. Similar results are obtained on examining the infusions obtained by treating the barley with ice-cold water. The reducing sugars, like the saccharose, increase continuously during germination, from 2.72 per cent. to 6.28 per cent., the curves representing the increase of the saccharose and the reducing sugars being parallel.

The only substance that diminishes continually during the germination of the barley is starch, and this fact affords further support to the conclusion of Brown and Morris that, under certain conditions, saccharose is formed at the expense of starch. C. H. B.

**The Bleeding of Plants.** By A. WIELER (*Bied. Centr.*, 22, 758—763; from Cohn's *Beitr. zur Biol. d. Pflanzen*, 6).—In the present paper, the term bleeding is used not only to denote the secretion of sap from wounds, but also the secretion from leaves and from fungi, &c. At present, there are 439 varieties of plants known to be capable of bleeding; probably further investigations will show it to be a property of all plants, or, at least, all phanerogams. As regards the parts of plants which bleed, it occurs in all parts of the roots and most above-ground organs. Temperature plays an important part. Experiments in which young plants of *Hordeum vulgare* (which, like most *Gramineæ*, bleed at the points of the leaves) showed that when the surrounding air is replaced by an indifferent gas (hydrogen) the bleeding ceases, but begins again as soon as oxygen is admitted. This would indicate that bleeding depends on a direct process of oxidation. In presence of chloroform or nitrobenzene, the bleeding is more or less checked, so that it seems likely that changes which give rise to bleeding are not purely chemical.

Many plants show certain periods during which they bleed, with intermediate periods when no bleeding occurs. With other plants, the bleeding is almost continuous. Variations of the limits of the periods of bleeding occur with different plants of the same species. It is also possible, by the addition of certain compounds to the solution in which the plants are grown, to alter the bleeding period. Thus, glycerol (1—2 per cent.), cane sugar (5—10 per cent.), potassium and ammonium nitrates, sodium phosphate, magnesium sulphate, iron sulphate, hydrochloric and citric acids, methyl-violet (0·0001 per cent.), caffeine,  $\frac{1}{2}$  per cent., and quinine hydrochloride ( $\frac{1}{2}$  per cent.) are favourable to bleeding. Bleeding is also increased by exposure to a temperature of 37—39°; a temperature of 19—20° is insufficient, so that the commencement of bleeding in the spring cannot be caused by the increasing warmth. There seems to be no connection between bleeding and new root production. The author's experiments confirm Hofmeister's law, that the minimal bleeding is in the morning and the maximum in the afternoon. It is impossible, at present, to say whether the daily bleeding is induced by light.

N. H. M.

**Production of Crystals of Calcium Oxalate in Vegetable Cell Membranes.** By H. K. MÜLLER (*Bied. Centr.*, 22, 786; from *Bot. Centr.*, 1892, 111).—The crystals are generally deposited within the membrane without contact with the cell-contents, but are sometimes formed inside the cells, and subsequently gradually enclosed in the membrane. The question as to the chemical process involved in the production of the crystals remains undecided, but it seems likely that they are formed by the contact of a soluble oxalate and a calcium salt in the membrane.

N. H. M.

**Calcium Oxalate in Plants.** By H. WARLICH (*Bied. Centr.*, 22, 786—787; from *Bot. Centr.*, 1892, 113).—Deposition of calcium oxalate occurs during the growth of leaves, and probably, also, when the leaves have ceased to grow. Oxalic acid is the solvent. In experiments with *Vanilla planifolia*, it was found that Wakker's "elaioplasten" became doubly refractive as they become older, and that at this period there are no crystals present. After treatment with dilute sulphuric acid, they are no longer doubly refractive. With increasing age, the crystals form from cell to cell, until, in still older leaves, they are generally close together, and at last the "elaioplast" disappears.

Calcium oxalate is sometimes redissolved in the plant.

N. H. M.

**Amount of Ethereal Thiocarbimides obtained from Rape Cake.** By ULBRICHT (*Bied. Centr.*, 22, 732—733).—The thiocarbimides found in rape cakes are due not only to the seeds of foreign *Crucifera*, but also to home-growing plants; if cakes contain more than 0·5 per cent. of the oil, it should only be given in the dry state, and even then, not to pregnant or milking animals.

Rape seed itself contains only one-half, and even less, oil than is contained in the cake, and this is believed to be due to the heating at 70° necessitated by the process of manufacture.

E. W. P.

**Indian Water-chestnut.** By D. HOOPER (*Pharm. J. Trans.*, 53, 22—23).—The Indian water-chestnut (*Trapa bispinosa*), an aquatic plant extensively cultivated in the North-West Provinces of India, yields nuts whose white kernels are roasted and pounded to a flour, which is largely used as a food. The author's analysis of the powdered kernels gave the following results in 100 parts:—fat, 0.97; sugar and gum, 14.36; albuminous matter, 8.41; starch, 63.84; cellulose, 3.60; ash, 4.66; water, 4.16. The substance contained 1.33 per cent. of nitrogen, and the "nutrient-ratio," that is, the ratio of albuminous to starchy matters, was 1 : 9.5; the nutrient value, 80.4. It is, therefore, as a food, comparable with the cereals, and is better than cleaned rice, which has the nutrient ratio of 1 : 10.8. The *Trapas* have been noted for their power of taking up manganese; thus Gorup-Besanez found 1.61 per cent. of manganese oxide in the whole plant of *Trapa natans*. The author found in the above-mentioned 4.66 per cent. of ash from the edible portion, only a very small quantity of manganese, but the pericarp was very rich in that metal.  
R. R.

**Composition of Russian Barley.** By V. TISHTCHENKO (*J. Russ. Chem. Soc.*, 25, 163—169).—The author has compiled, from his own observations and other data, a table giving the amount of proteid matter (nitrogen  $\times$  6.25) in 62 samples of barley grown in different districts of Russia and used for brewing purposes. In some cases, the moisture, starch, ash, and phosphoric acid are also given. He finds that the nitrogen of crops grown in the same district in different years is fairly constant, and that three characteristic types may be distinguished. Polish barley contains 10—11 per cent. of albuminous matter; Tzaritzinsk (Don district), barley, 15 per cent.; and Tcherimiss (upper Volga and Kama), barley, 12 per cent.; the mean percentage for barley grown in Western Europe being from 10.5 to 11.5.  
J. W.

## Analytical Chemistry.

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**Detection of Chlorine, Bromine, and Iodine in the same Mixture.** By J. TORREY (*J. Anal. and Appl. Chem.* 6, 667—669).—The author has slightly modified the process originated by Hart and communicated by Kebler. The bulb tube arrangement has been replaced by a small tube having only one small bulb blown on it, the tube being bent slightly away from the perpendicular about half an inch above where it leaves the cork. Above the bulb there should be about half an inch of tube left. The flask containing the mixture is charged with ferric sulphate as usual, and the iodine evolved is readily detected by holding in the steam a small piece of starch-paper. When iodine fumes can no longer be detected, a crystal of potassium permanganate is added, and, on further heating, bromine

is given off, which is best detected by allowing the fumes to act on iodised starch paper. The boiling must be quite brisk, or else the bromine will not be completely expelled. The residue is then tested for chlorine in the usual manner. The author advises working on a very small quantity of substance.

L. DE K.

**Titration of Caustic Liquors containing Chlorine.** By C. ULLMANN (*Chem. Zeit.*, 17, 1208—1209).—A measured quantity of the lye is mixed with an excess of standard solution of succinic acid and heated until the odour of hypochlorous acid has gone off. The excess of acid is then titrated with standard soda, using phenolphthaleïn as indicator.

Succinic acid expels carbonic anhydride and hypochlorous acid, but is without action on chlorides, and is also proof against oxidising or chlorinating agents.

L. DE K.

**Estimation of Nitrogen in Manures containing Nitrates.** By V. SCHENKE (*Chem. Zeit.*, 17, 977—979).—After reviewing a large number of processes, the author finally recommends the following, which is really a combination of Kjeldahl and Ulsch's processes. A few grams of the sample is introduced into a 300 c.c. flask, and treated with about 4 grams of reduced iron and some 10 c.c. of dilute sulphuric acid (1—2). After applying a gentle heat to complete the reduction, a sufficiency of sulphuric acid containing 20 per cent. of phosphoric anhydride is added, and also a little copper oxide. The mixture is now further treated as in Kjeldahl's process.

L. DE K.

**Reaction of Hydroxylamine.** By A. ANGELI (*Gazzetta*, 23, ii, 102).—A new reaction for hydroxylamine consists in adding to its neutral aqueous solution first sodium nitroprusside, then caustic soda; on boiling the mixture, it becomes coloured a fine magenta red. The red colour produced by phenylhydrazine under similar conditions disappears on heating. The test is very sensitive, but should not be applied to solutions containing a large excess of ammonium salts.

W. J. P.

**Estimation of Yellow Phosphorus.** By G. TÓTH (*Chem. Zeit.*, 17, 1244—1245).—The phosphorus is dissolved in carbon bisulphide, and the solution is diluted with olive oil and agitated with solution of silver nitrate. The argentic phosphide thus obtained is oxidised by means of dilute nitric acid, and the aqueous layer is separated from the oil.

The phosphoric acid is now estimated by the molybdate method and calculated to phosphorus. In four test experiments, 78, 93, 93 and 100 per cent. of phosphorus was respectively recovered.

L. DE K.

**Estimation of Sulphur in Steel, Iron, &c.** By H. A. HOOPER (*Chem. News*, 68, 191).—The steel or iron is dissolved in hydrochloric acid, and the sulphur, evolved as hydrogen sulphide, is absorbed in caustic soda and subsequently titrated with a standardised solu-



tion of lead nitrate. Rapidity and delicacy are claimed for the method. D. A. L.

**Volumetric Estimation of Lead.** By A. P. LAURIE (*Chem. News*, 68, 211).—To estimate lead in the presence of hydrochloric acid, it is directed to neutralise the acid, add sodium acetate, avoiding large quantities of other salts, then to titrate with standardised potassium dichromate, made up to precipitate 0.002 gram of lead per c.c., using silver nitrate as indicator, a yellow tint in the precipitate of silver chloride indicating the end of the reaction. The sensitiveness is influenced by the proportion of chloride present, the most satisfactory amount being from 0.5 to 0.2 gram of sodium chloride in 100 c.c. To obviate inconvenience, arising from the formation of basic salts and from floating particles of lead chromate, most of the required quantity of dichromate is added at once, and the liquid is gradually heated to boiling with frequent stirring. D. A. L.

**Assay of Copper Sulphate.** By J. RUFFLE (*Analyst*, 18, 279—281).—The author estimates the copper electrolytically, and calculates it into the crystallised sulphate. This, on being heated at 100° to constant weight, loses 28.91 per cent. of water. If now a sample loses more water than corresponds with the copper sulphate it contains, the excess may be put down to adherent moisture.

For the purpose of estimating any free sulphuric acid, 20—50 grams of the sample is powdered and repeatedly extracted with absolute alcohol. The alcoholic filtrate is diluted with water, mixed with a few drops of phenolphthaleïn, and titrated with standard soda.

L. DE K.

**Separation of Copper from Cadmium by the Iodide Method.** By P. E. BROWNING (*Amer. J. Sci.*, [3], 46, 280—283).—The author recommends the following modification of the iodide process. The solution containing the two metals is mixed with potassium iodide as long as a precipitate forms, and the liberated iodine is boiled off. The cuprous iodide is collected on a weighed asbestos filter, washed, dried at 120—150°, and weighed. The filtrate is heated with potassium nitrite and sulphuric acid to decompose the excess of iodide, and when every trace of iodine is expelled, the cadmium is precipitated by boiling with sodium carbonate. The cadmium carbonate is next collected on an asbestos filter, and converted into oxide by ignition.

The test analyses are extremely satisfactory.

L. DE K.

**Quantitative Analysis by Electrolysis.** By A. CLASSEN (*Zeit. anorg. Chem.*, 5, 231—236).—A rejoinder to Rudorff (*Abstr.*, 1893, ii, 391).

**Effect of Platinum in Iron Solutions.** By R. W. MAHON (*Amer. Chem. J.*, 15, 578—582).—When the insoluble residue of an iron ore is fused with sodium carbonate in a platinum crucible, and the melt dissolved in hydrochloric acid, some platinum, usually about 1 milligram, goes into solution, and this affects the estimation of the iron with standard dichromate, in the case when the iron is reduced to the

ferric state by means of stannous chloride, the excess of the latter being removed with mercuric chloride. The platinum chloride functions continuously, undergoing a cycle of changes the net result of which is to oxidise the ferrous to ferric chloride at the expense of mercuric chloride, which is reduced to mercurous chloride. The error introduced may thus be large; it is increased by protracted fusion, by the presence of much free hydrochloric acid, or by the addition of a large excess of stannous chloride. It may be made small by avoiding these conditions; but, to ensure an accurate result, it is best to free the iron from platinum by precipitating it with ammonia, and redissolving the washed precipitate in hydrochloric acid.

C. F. B.

**Estimation of Ferric Oxide and Alumina in Mineral Phosphates.** By G. MARIANI and E. TASSELLI (*Staz. Sper. Agrar.*, 23, 31—37).—The method of estimating ferric oxide and alumina by precipitating the phosphates with ammonia and acetic acid has been almost entirely superseded by Glaser's method (*Abstr.*, 1890, 420), on account of the partial precipitation of lime and the partial solubility of the phosphates in the acetic acid. Another cause of error which seems to have been overlooked is the sparing solubility of ferric orthophosphate in hot water (Sestini, *Staz. Sper. Agrar.*, 1875). The following modification is recommended as giving accurate and concordant results as shown by experiments with solutions of known strength. Glaser's method gave somewhat lower results except with basic slag; in this case, however, the results were higher, owing to the presence of manganese, which is liable to be precipitated with the iron and aluminium.

The phosphate (1—5 grams) is boiled with hydrochloric acid (15 c.c.) for about 10 minutes, diluted with water (2 parts), and oxidised by means of crystals of potassium chlorate and a few drops of nitric acid, the whole being boiled to expel most of the chlorine. It is then filtered, washed, the filtrate made up to about 150 c.c., and a solution of ammonium phosphate (0.5 gram) added, then glacial acetic acid (2 c.c.) and, drop by drop, ammonia until a slight permanent precipitate is produced, after which slightly ammoniacal water is gradually added until a slightly alkaline reaction is obtained; acetic acid (2 c.c.) is now added, the whole shaken, and left for two hours. The clear liquid is decanted through a filter, the precipitate being washed with a 1 per cent. solution of ammonium phosphate; the funnel containing the precipitate is put over the same flask, and the precipitate redissolved by pouring on, drop by drop, hydrochloric acid (sp. gr. 1.12). After washing the filter sufficiently, the iron and alumina are again precipitated as before, then left for an hour, decanted through a filter, washed with ammonium phosphate solution, dried, ignited (with filter) at a dull red heat, and weighed.

This modification gives as good or better results than Glaser's, but it may be possible to improve the method still further.

N. H. M.

**Estimation of Chromium in Ferrochrome.** By J. SPÜLLER and S. KALMAN (*Chem. Zeit.*, 880, 1207—1208).—The authors mix 0.35 gram of the finely-powdered substance with 8 grams of sodium hydroxide and  $\frac{1}{4}$  grams of sodium peroxide, and ignite for about an hour in a silver dish with occasional stirring. After cooling, the mass is dissolved in water, and any sodium ferrate or manganate decomposed by adding more sodium peroxide; the excess of the latter being removed by passing a current of carbonic anhydride, and gently warming. The chromate is then estimated by means of a ferrous salt according to Schwarz's method. L. DE K.

**Assay of Tin Ores.** By H. W. RENNIE and W. H. DERRICK (*J. Soc. Chem. Ind.*, 11, 662—667).—The ore is pulverised until it will pass through a sieve of 60 meshes, or for low grade ores containing much iron one of 90 meshes, to the linear inch; 250 grains of it is then boiled for half an hour with 3 oz. of hydrochloric acid and  $\frac{1}{2}$  oz. of nitric acid, and the residue carefully washed by decantation; wolfram, if present, may be dissolved out by ammonia. The residue is then washed on a vanning shovel, when, by skilful manipulation, the free silica can be washed away without the loss of a trace of tin, leaving nearly pure cassiterite. In many cases the percentage of cleaned cassiterite furnishes sufficient information, but when it is required to know the actual percentage of tin, 50 grains of this oxide is reduced by potassium cyanide with the following precautions. The cyanide should be pure and finely powdered, and both it and all the apparatus should be thoroughly dry; crucibles about 3 in. high, of a fine-grained clay and of a smooth interior, should be used, otherwise numerous minute prills of tin adhere to the crucible and cannot be collected. A layer of cyanide is first rammed into the crucible, then the mixture of oxide with 300 grains of cyanide, and finally a covering of cyanide. The crucible, closely covered, is then placed in a muffle, already at a low red heat that the cyanide may fuse rapidly, but not froth. After 10 minutes, the crucible is gently shaken to wash down prills from the sides; the heat is then raised to a bright red for another five minutes. The traces of silica present form a globule of greenish slag, less fusible than the cyanide. As the temperature is raised, this detaches itself from the metal and rises to the surface. As soon as this has occurred, the crucible is allowed to cool, and its contents treated with boiling water, when the button of metal is left in a state fit for weighing. The results leave nothing to be desired in point of accuracy. M J. S.

**Separation of Copper from Bismuth.** By E. F. SMITH (*Zeit. anorg. Chem.*, 5, 197—198).—A rejoinder to Classen (*Abstr.*, 1893, i, 495).

**Separation of Copper from Bismuth.** By A. CLASSEN (*Zeit. anorg. Chem.*, 5, 299).—A reply to Smith, who has pointed out an error in the author's work on electrochemical analysis.

**Quantitative Separation of Metals in Alkaline Solution by means of Hydrogen Peroxide.** By P. JANASCH and J. LESINSKY (*Ber.*, 26, 2908—2912: compare this vol., ii, 32).—*Separation of Bismuth from Copper.*—Bismuth and copper (about 0.3 gram of each) are dissolved in concentrated nitric acid (5 c.c.), diluted with water (50 c.c.), and the bismuth precipitated by means of a mixture of 3 per cent. hydrogen peroxide (50 c.c.) and concentrated ammonia (15 c.c.), care being taken to avoid loss by frothing. The precipitate is washed first with a mixture of hydrogen peroxide (2 vols.), concentrated ammonia (1 vol.), and water (8 vols.), secondly with warm dilute ammonia (1:8), and finally with hot water; the complete removal of the copper is attained with difficulty. The bismuth oxide is dried at 90—95°, ignited with the filter paper in a platinum dish, and the residue dissolved in nitric acid, and ignited until its weight is constant. The copper, after conversion into sulphate and removal of the nitric acid, is precipitated by the prolonged action of hydrogen sulphide, and the precipitate converted into oxide by ignition in a stream of oxygen. The analytical results show that the amount of bismuth obtained is in excess of the theoretical by 0.2—0.3 per cent. Heating the liquid immediately after the precipitation of the bismuth appears to be without marked result, except that traces of copper are retained by the bismuth oxide, and can only be removed by redissolving it and reprecipitating. The addition of hydroxylamine (*Abstr.*, 1893, ii, 500) is attended by a similar result, the bismuth oxide being deposited as a white, crystalline powder. J. B. T.

**Estimation of Gold and Silver in Antimony or Bismuth.** By E. A. SMITH (*J. Soc. Chem. Ind.*, 12, 316—319).—*Assay of Antimony for Gold and Silver. 1st Method.*—The sample is powdered in an iron mortar, passed through a sieve of 80 holes to the linear inch, and well mixed. 500 grains of the powder is then mixed with 3000 grains of litharge, put into an earthen crucible, and fused in an air furnace, the crucible being partly covered during the operation, which lasts about 15 minutes. The melt is poured into an ingot, and, after cooling, detached from the slag. The lead button, although a little hard, is malleable, and, after being scorified to a convenient size, it may be cupelled in the ordinary way. The gold is afterwards parted from the silver by means of nitric acid. When assaying samples fairly rich in gold or silver, small quantities of the precious metals may be retained by the slag. The latter should therefore be again fused with 500 grains of litharge and 20 grains of charcoal, and the lead button thus obtained cupelled as before.

*2nd Method.*—500 grains of the sample of antimony is fused with 1000 grains of litharge, 200 grains of nitre, and 200 grains of sodium carbonate. The fusion is generally complete in 15 minutes, and the buttons of lead may be at once cupelled without previous scorification, thus saving considerable time. The test analyses are satisfactory.

*Assay of Bismuth.*—The metal is melted under a layer of charcoal, and, after adding a piece of resin, it is poured into moulds so as to

obtain buttons weighing about 500 grains. After adjusting them to exactly 500 grains, they are at once carefully cupelled in a muffle at a slightly lower temperature than that employed for the cupellation of lead. The resulting buttons of gold and silver are then treated as before with dilute nitric acid. L. DE K.

**Sodium Peroxide in Water Analysis.** By S. RIDEAL and H. J. BULT (*Chem. News*, 68, 190—191).—It is found that on treating potable water, or water contaminated with fresh sewage, with sodium peroxide (in a solution containing 2 grams per litre) instead of with alkaline permanganate, only part of the organic matter is attacked, and, consequently, after such treatment, the waters yield a further quantity of ammonia with permanganate; this residual organic matter is, however, much more readily oxidised than the organic matter that has not been treated with the peroxide. D. A. L.

**Amount of Glucose in Beets and in Diffusion Juice.** By H. CLAASSEN (*Bied. Centr.*, 22, 769—771).—The percentage of glucose present in beet-root should be estimated in the root itself and not in the expressed juice.

Slices of the root are digested in water, basic lead acetate is added (not in excess), and the whole further digested; the solution is then neutralised by calcium carbonate, in order that there may be no free alkali. After filtration, the lead is precipitated by soda, and the sugar present estimated by means of Fehling's solution.

E. W. P.

**Estimation of Glycogen.** By J. WEIDENBAUM (*Pflüger's Archiv*, 54, 319—332).—The research consisted in a critical investigation of Fränkel's method of separating and estimating glycogen (*Abstr.*, 1893, i, 386).

The glycogen obtained by this method is very impure; dissolved in dilute potash, it gives, after neutralisation with hydrochloric acid, a fairly heavy precipitate with Brücke's reagent. The longer the organ is treated with trichloroacetic acid, the greater is the nitrogen present in the so-called glycogen extracted; in some cases, almost half the substance is proteid. The residue, also, is not freed from glycogen by the extraction, nearly a third of the total glycogen being left behind. W. D. H.

**Colour Reaction of Phenylhydrazine on Lignin and Aldehydes.** By E. NICKEL (*Chem. Zeit.*, 17, 1209, 1243—1244).—Wood, immersed in a solution of phenylhydrazine hydrochloride, turns pale yellow, the colour deepening on the addition of dilute hydrochloric acid. After the lapse of an hour, or sometimes several hours, the colour changes to a distinct green. Wood, and particularly bamboo, immersed in a solution of hydrazine sulphate, acquires, after a few minutes, a clear yellow colour, which turns orange on adding hydrochloric acid.

Hydrazine sulphate, added to a solution of vanillin, produces a deep yellow coloration, but no precipitate; the addition of hydrochloric acid gives a flocculent, yellow precipitate, but this did not turn orange.

Piperonal, parahydroxybenzylaldehyde, and salicylaldehyde give similar colorations.  
L. DE K.

**Estimation of Oxalic acid.** By A. GUNN (*Pharm. J. Trans.*, 53, 408—410).—The author proposes to use the yellow colour of ferrous oxalate as a means of determining oxalic acid in certain cases where the ordinary methods are not readily applicable. Absolute accuracy is not claimed for the process, but it appears to be specially useful for estimating oxalic acid when mixed with tartaric acid. The solution of ferrous salt preferred is that of the phosphate, which is nearly colourless, and the determination is made colorimetrically by comparison in Nessler glasses with a standard solution. The colour is destroyed by the strong mineral acids, and the reaction is also interfered with by the presence of much alum. The results are improved by a preliminary neutralisation of the acids by ammonia. Coloured solutions may be first treated with animal charcoal, and any residual tint allowed for in the comparison.  
R. R.

**Estimation of Tannin and Gallic acid.** By W. P. DREAPER (*J. Soc. Chem. Ind.*, 12, 412—415).—The author recommends the following process. The solution containing the tannin and gallic acid is heated to 80°, and, after adding some pure barium carbonate, a standard solution of copper sulphate is added until a drop of the supernatant liquid gives a faint brown coloration when mixed with potassium ferrocyanide. Another portion of the solution is precipitated by means of gelatin, and, after filtering, the titration is repeated. The difference in c.c. of copper solution between the two estimations is the measure for the amount of tannin. The copper solution should, of course, be checked with pure tannin and also with gallic acid, as the latter requires a much larger amount of copper for precipitation than tannin does.  
L. DE K.

**Analysis of Tanning Materials.** By A. GAWALOWSKY (*Zeit. anal. Chem.*, 32, 618—619; from *Drester'ski's Handwörterbuch für Pharmacie*).—An extract of the material is precipitated with the smallest possible excess of copper acetate, and after a time is filtered by suction through a dried and weighed filter; the precipitate is washed with cold water, dried until the weight is constant, and incinerated. The ash is dissolved in nitric acid and again ignited to determine the copper as oxide. The difference gives the total tannin, gallic acid, pectin, &c. Another part of the extract is evaporated to a syrup, treated with alcohol-ether (2 : 1), and the pectin with traces of albumin and casein filtered off; the alcohol-ether is evaporated from the filtrate, and the residue dissolved in hot water and filtered from fat and resin. The cold filtrate is now mixed with copper acetate and ammonium hydrogen carbonate; this precipitates the tannin, leaving copper gallate in solution. The pectin precipitate is dissolved from the filter with hot water, and the cooled solution precipitated with copper acetate. Both these precipitates are treated like the former one; the gallic acid is then known from the difference.  
M. J. S.

**Separation of Uric acid from Xanthine.** By J. HORRACZEWSKI (*Zeit. physiol. Chem.*, 18, 341—350).—In view of a certain amount of hostile criticism which has followed the publication of the author's views on the origin of uric acid in the organism from nuclein, he admits that the separation of uric acid from xanthine bases is difficult. Artificial mixtures of uric acid and xanthine showed a loss of uric acid when that substance was estimated by Fokker's method. The separation of the two substances by means of hydrochloric acid led to better results; but there is still a noteworthy loss. By means of concentrated sulphuric acid, the mixture being allowed to stand five hours, the loss is inconsiderable, the greatest difference being 0.005 gram. If longer than five hours is allowed to elapse, some xanthine is precipitated also.

The same method was successfully carried out in the separation of uric acid from guanine. W. D. H.

**Precipitability of Uric acid and Bases of the Uric acid Group as Cuprous Oxide Compounds.** By M. KNÜGER (*Zeit. physiol. Chem.*, 18, 351—357).—By the use of copper sulphate and sodium hydrogen sulphite, all xanthine-like substances which contain a substituted NH-group are precipitated from hot solutions as compounds with cuprous oxide. Theobromine is a noteworthy exception. As a quantitative method, it is as good as ammoniacal silver solution. The use of sodium thiosulphate as a reducing agent gives a means of separating adenine and hypoxanthine, and probably also of guanine and xanthine. W. D. H.

**Assay of Naphtholsulphonic and Naphthylaminesulphonic acids.** By W. VACBEL (*Chem. Zeit.*, 17, 1265—1266).—The sulphonic acids may be divided into three classes:—1. Those which generally absorb only 1 atom of bromine; 2. Those which slowly absorb several atoms of bromine; 3. Those which do not combine with bromine at all. Only those of the first class can be readily assayed by the author's process. They comprise: *a*, naphthionic acid; *b*, Dahl's disulphonic acid II; *c*, Dahl's disulphonic acid III; *d*, paramonosulphonic acid (2Br); *e*, naphthylenediaminemonosulphonic acid.

The analysis is carried out by dissolving a known weight of the compound in water, and adding excess of potassium bromide and dilute sulphuric acid. Standard solution of potassium bromate is then added from the burette until the liquid contains free bromine.

L. DE K.

**Hübl's Iodine Absorption Process.** By W. FAHRION (*Chem. Zeit.*, 17, 1100).—The author (*Abstr.*, 1893, ii, 103) has demonstrated that the action of Hübl's reagent on oils is not quite so simple as has been supposed, and that iodine is also absorbed by other fatty constituents. In this view, the author is supported by Gantter, who has found that even saturated fatty acids combine with iodine.

The author has tried to improve the process by substituting methylic alcohol for ethylic alcohol in preparing the reagent, but,

excepting the fact that the solution keeps better, no special advantage accrues therefrom.

L. DL K.

**Reducing Action of Rancid Fat and Lard on Silver Nitrate.** By G. MARIANI (*Staz. Sper. Agrar.*, 23, 355—359).—Experiments were made with Brullé's nitrate of silver test for margarine (Abstr., 1891, 506). Pure butter gave no colour, and pure margarine did not give the red colour mentioned by Brullé. But in presence either of rancid butter or rancid margarine there was either a blackish deposit or a mirror, according to the degree of rancidity. Fresh hog's fat, on the other hand, reduced the silver salt, acquired a more or less intense red colour, and formed a brownish deposit.

An examination of the deposits obtained on the one hand from rancid butter and margarine, and from fresh lard on the other, showed that, whilst the former consisted of silver oxide and silver, the latter contained sulphide as well as oxide of silver. It is thus seen that lard, like the oils of some Cruciferae, contains sulphur. In confirmation of this it was found that Benedikt's reaction for colza (*Anal. d. Fette*, 227) is also shown by lard.

The reaction is thus useless for the detection of margarine in butter.

N. H. M.

**Pennetier's Method for detecting Margarine in Butter.** By A. PIZZI (*Staz. Sper. Agrar.*, 22, 131—137, and 23, 35—43).—Several examinations, by Pennetier's microscope-polariscope method, of pure butter and butter mixed with various amounts of margarine were made, the results of which are shown in a coloured plate. An examination was also made of the fat of natural butter, which was obtained by melting the butter, allowing it to partially solidify, and separating the solid portion; this, when examined with the polariscope, showed a red ground with detached yellowish and greenish particles, whilst ordinary butter shows a red ground mostly covered with a confused mass of various colours.

Some of the objections to Pennetier's method are the difficulties introduced by conditions of temperature, the effect of added crystalline and amorphous substances, and the manner in which the margarine may have been mixed with the butter. As regards the first, the author observed no difference between butter which had been melted and cooled quickly and butter which had been slowly cooled. With butter containing margarine which had been kneaded in, the method, gives good results, but when churned with the butter the mixture behaved like pure butter.

Very rancid and mouldy butter gave the margarine reaction. The inner portions of rancid butter, which had no mould on the surface, gave a negative optical reaction, whilst the outer portions gave a positive reaction.

M. G. H.

The method will show the presence of margarine, but is limited in its application.

N. H. M.

**Estimation of Nicotine in Tobacco.** By R. KISSLING (*Zeit. anal. Chem.*, 32, 567—571).—The author vindicates his method against the strictures of Vedródi (Abstr., 1893, ii, 504), and asserts



that if his instructions are accurately followed, the ethereal extract will contain no ammonia, that no nicotine will be lost during the distillation of the ether, and that the results of his method agree closely with those of Popovici (Abstr., 1889, 802). The extraction with ether should, however, follow as quickly as possible the addition of the soda to the tobacco, as otherwise a loss of nicotine may take place.

M. J. S.

**Furfuraldehyde Reactions of Alkaloids.** By N. WENDER (*Chem. Zeit.*, 17, 950—951).—When two or three drops of a mixture of sulphuric acid and furfuraldehyde (5 drops to 10 c.c. acid) is added to a minute particle of an alkaloid, a characteristic colour makes its appearance, and the author has tabulated the results. The method is, however, only of distinct value in the case of veratrine. This, when rubbed with a glass rod moistened with the reagent, gives first a yellowish-green, and then an olive-green mixture; the edges, and the whole of the mixture afterwards, turn a beautiful blue. On warming, the mixture gradually acquires a purple-violet colour. The blue substance obtained in the cold is insoluble in alcohol, ether, or chloroform. The least amount of water, or alkali, decolorises the solution, and on adding much water a fairly permanent yellow solution is obtained.

Excepting sabadilline, no other alkaloid gives the reaction, although the test with that alkaloid is not quite so satisfactory. If instead of sulphuric acid other acids are used, the reaction does not manifest itself.

L. DE K.

**Estimation of Nitrogen and Proteids in Milk and its Products.** By L. CARCANO (*Staz. Sper. Agrar.*, 22, 261—263).—According to L'Hôte (Abstr., 1889, 438 and 746), and Oddy and Cohen (Abstr., 1890, 1466), Kjeldahl's method is not suitable for certain substances; with some, it gives coloured solutions after prolonged heating, and low results are obtained owing to incomplete oxidation, and to loss of ammonium sulphate during the heating. Menozzi, and also Musso (*Gazzetta*, 6), estimated nitrogen in milk and its products by Dumas', and by Will and Varrentrapp's methods; they both found that the Will and Varrentrapp method gave low results (compare also Violette, Abstr., 1889, 546, and Aubin and Alla, *ibid.*, 648 and 925).

The author estimated the nitrogen in milk, Emmenthaler cheese, and cheeses prepared from mare's milk and from sheep's milk, &c., employing both Dumas' and Kjeldahl's methods. Proteids were also determined in milk by Ritthausen's method. The modification of the Kjeldahl process was that recommended by the Directors of the Italian Agricultural Stations, with due regard to precautions mentioned by Zecchini and Vigna (Abstr., 1889, 649), and by Proskauer and Zülzer (*Chem. Centr.*, 1885, 17). In every case except one, the Kjeldahl results were somewhat lower than those obtained by Dumas' method, but the difference was generally very slight.

For milk analysis, the Kjeldahl process is much less troublesome than Dumas' method, and, although somewhat slow, several determinations can be carried on at once.

N. H. M.

## General and Physical Chemistry.

**Observations on Optical Rotation.** By J. A. LE BEL (*Bull. Soc. Chim.*, [3], 9, 674—680).—The experiments recorded in this paper were made to throw light on the law of the change of sign when the radicles of optically active compounds are replaced by others, notably by acidyl groups and halogen atoms. The author enters at length into his own theoretical views and those of GUYE. His conclusions are not definite, but he states that the optical action appears to increase with the mass (GUYE's hypothesis).

Methylpropylcarbinol is prepared by the hydrogenation of the mixed ketone obtained by distilling calcium acetopropionate. After growing *Penicillium glaucum* in its solution, it becomes lævorotatory; the chloride is slightly dextrorotatory, and the iodide more so. The tartaric chlorhydrins, methylpropylcarbinol and its derivatives, as well as ethylpropylcarbinol, were examined. The iodide from the last compound is lævorotatory, not dextrorotatory, as stated (*Abstr.*, 1893, i, 246). Derivatives of methylamylcarbinol, propylglycol, the ethereal lactates, and isobutylamyl ether were also examined. A. R. L.

**Electromagnetic Rotation of the Plane of Polarisation of some Acids and Salts in different Solvents.** By O. HUMBURG (*Zeit. physikal. Chem.*, 12, 401—415).—In order to ascertain whether a connection exists between the magnetic rotation of an electrolyte and its electrolytic dissociation, a number of fatty acids and of inorganic salts were examined in solution in water and in other solvents. Benzene and toluene were used as solvents for the fatty acids, and methylic alcohol for the salts examined. The rotation of the fatty acids is independent of the solvent, and is the same in aqueous solution, in benzene, and in toluene; this holds even in the case of the chloracetic acids, which must be regarded as strongly dissociated in aqueous solution. The inorganic salts taken were potassium iodide, sodium and barium bromides, and ammonium nitrate. The molecular conductivities of these salts is much smaller when measured in the methylic alcohol solutions than in water, and, therefore, as was to be supposed, the dissociation is relatively much smaller in the first case. The rotation, however, remains practically unchanged with change of solvent, showing that it is independent of the dissociation. From the results of these experiments, therefore, it appears that electrolytic dissociation has no appreciable influence on the magnetic rotation.

The rotations of chlorine and bromine derivatives of some of the fatty acids and of some hydrocarbons were measured, and from these the atomic rotations of chlorine and bromine were calculated. The numbers obtained were, for chlorine 1.606 in the case of the fatty acid derivatives, and 1.675 from hydrocarbon derivatives; for bromine, 3.525 and 3.563 in corresponding cases. The numbers are practically identical in the two series. H. C.

**Optical Rotation and Electrolytic Dissociation.** By H. HÄDRICH (*Zeit. physikal. Chem.*, 12, 476—497).—According to Oudemans, the molecular rotation of salts in dilute solution is independent of the character of the inactive ion of the salt, a result which is in full accordance with the electrolytic dissociation theory. This view has been called in question, notably by Frankland (*Trans.*, 1893, 312), and in this paper the author submits it to further experimental investigation. The salts examined were, in the first instance, those of the alkaloids morphine, quinine, conquinine, cinchonidine, brucine, and strychnine. In each case in sufficiently dilute solution, the rotation is found to be independent of the inactive acid, and, therefore, the same for the different salts of any one alkaloid. This is also true of the methylammonium salts of the alkaloids. In these cases, therefore, the law of Oudemans is fully confirmed. Boryl, arsenyl<sup>1</sup>, and antimonyl tartrates were also examined, and these in dilute solution are found to obey Oudemans' law. The rotation of these salts differs from that of the other tartrates, and therefore the active ion is not that present in tartaric acid itself.

H. C.

**Reverberatory Electrical Furnace with Movable Electrodes.** By H. MOISSAN (*Compt. rend.*, 117, 679—682).—The furnace consists of a parallelopiped of Courson limestone, in which is cut a somewhat large cavity, also a parallelopiped in shape, which is lined with alternate plates of magnesia and carbon, about 10 mm. thick, so arranged that magnesia is in contact with the limestone, whilst carbon forms the internal lining of the cavity. A lid, of alternate plates of magnesia and carbon, covers the cavity, and a block of Courson limestone is placed above this lid. The electrodes are movable, and pass through slots cut in opposite sides of the furnace. At right angles to the electrodes a carbon tube, 10 to 20 mm. in diameter, passes through the furnace, and is so arranged as to be 10 mm. below the arc, and 10 mm. above the bottom of the cavity. If necessary, the tube can be lined with magnesia. By inclining the tube at an angle of about 30°, the furnace can be made to work continuously, the reducible material being introduced at the higher end, whilst the product of reduction is drawn off at the lower end. With a current of 600 ampères and 60 volts, 2 kilos. of fused metallic chromium can be obtained in about an hour, the metal being received in a crucible made of chromic oxide. The metal is white, finely granular, and very hard, and takes a high polish.

The magnesia is prepared by heating strongly the basic carbonate, digesting the product with ammonium carbonate solution, and again strongly heating. It is then moistened with water and compressed.

With this furnace, silicon carbide and vanadium carbide can be readily obtained by the direct combination of carbon vapour with the vapours of silicon and vanadium.

C. H. B.

**Electrolytic Thermoelectric Cells.** By A. GÖCKEL (*Ann. Phys. Chem.*, [2], 50, 696—704).—The author has investigated the electromotive force of thermo-elements constructed on the following plan:

$\text{Hg} \mid \text{solid Hg salt} : \text{salt solution} : \text{solid Hg salt} \mid \text{Hg}$   
 cold hot

He finds that in general the thermoelectric force for 1° difference of temperature increases with dilution of the solution, and that in equivalent dilute solutions of similar salts of an acid it is practically the same. He confirms in general Ebeling's observation, that the worst conductors are thermoelectrically the most active, and that some show a maximum thermoelectric force at the concentration of maximum conductivity.

J. W.

**Velocity of Ions.** By F. KOHLRAUSCH (*Ann. Phys. Chem.*, [2], 50, 355—408).—In the present paper the author has collected and discussed all the available data bearing on the speed of electrolytic ions, the numerical values being made as far as possible comparable.

First, he gives a table of the Hittorf numbers for the anion of 23 electrolytes at different dilutions. He then shows that the speed of the chlorine ion is the same in solutions of the alkali chlorides at equivalent concentrations from semi-normal downwards, and that the speeds of the two ions of these and similar salts are additive in dilute solutions. As a first approximation, he considers that the increase of the molecular conductivity for the same amount of dilution of different salts is the same.

The following table of the molecular conductivity at infinite dilution and 15°, and the corresponding speeds of the ions is given. U and V denote the velocities of the kation and anion respectively in centimetres per second; u and v the velocities referred to mercury units;  $\lambda$  the conductivity at infinite dilution.

	$\lambda_{\infty}$ 10 <sup>-7</sup> .	u. 10 <sup>-7</sup> .	v. 10 <sup>-7</sup> .	U. 10 <sup>-3</sup> .	V. 10 <sup>-3</sup> .
KCl.....	123	60	63	66	69
NaCl.....	103	41	62	45	69
LiCl.....	95	33	62	36	69
NH <sub>4</sub> Cl.....	122	60	62	66	68
HCl.....	353	290	63	320	70
KI.....	123	60	63	66	69
KNO <sub>3</sub> .....	116	60	58	66	64
NaNO <sub>3</sub> .....	98	40	58	44	64
AgNO <sub>3</sub> .....	109	52	57	57	63
HNO <sub>3</sub> .....	350	(290)	(60)	(320)	(65)
KClO <sub>4</sub> .....	115	(61)	(51)	(67)	(60)
KC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> .....	94	63	31	69	34
NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> .....	73	41	32	45	35
KOH.....	222	55	165	64	181
NaOH.....	201	36	165	40	191
AgClO <sub>4</sub> .....	103	51	52	57	57
AgClO <sub>3</sub> .....	106	52	54	57	60
AgC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> .....	83	53	30	58	34
AgC <sub>2</sub> H <sub>11</sub> SO <sub>3</sub> .....	73	52	21	57	23

J. W.

**Electrical Conductivity of Cupric Chloride Solutions.** By R. J. HOLLAND (*Ann. Phys. Chem.*, [2], 50, 349—360).—Solutions of cupric chloride show a regularly diminishing rate of increase of the conductivity as the temperature rises, and then varies with the concentration, the maximum conductivity being obtained with a solution containing about 18 per cent. of anhydrous salt. The temperature coefficient varies with the concentration, and reaches a maximum at about 40°. J. W.

**Change of Conductivity of a Solution by the Addition of a Non-electrolyte.** By R. J. HOLLAND (*Ann. Phys. Chem.*, [2], 50, 261—292; compare Abstr., 1892, 1382).—The author gives the following account of his general results.

The electrical conductivity of a solution of an electrolyte in methylic alcohol diminishes on the addition of a non-conductor, the diminution varying with the nature of the non-electrolyte and with the degree of dilution. The four non-electrolytes benzene, toluene, xylene, and oil of turpentine diminish the conductivity in the order given. The diminution varies for each volume per cent. of non-electrolyte added from 1.7 to 2 per cent. of the conductivity of the corresponding normal solution for 0.01-normal solutions; 1.6—1.75 per cent. for 0.001-normal, and 1.4—1.6 per cent. for 0.0005-normal.

The temperature coefficients of alcoholic solutions increase with increasing dilution; are only half as great as in the case of aqueous solutions; and are very little affected by the addition of a non-conductor.

The conductivity of methylic alcohol solutions up to a concentration of 20 per cent. of non-electrolyte is very exactly represented by Arrhenius' formula (Abstr., 1892, 1038). No connection between electrical conductivity and fluid friction was evident. J. W.

**Heat of Dissociation in Electrochemical Theory.** By H. EBERT (*Ann. Phys. Chem.*, [2], 50, 255—260).—The molecular heat of dissociation of the hydrogen molecule into atoms, as calculated by E. Wiedemann, is about  $1.1 \times 10^{10}$  ergs; the same magnitude for iodine, calculated by Boltzmann from Meier and Crafft's data, is  $1.2 \times 10^{10}$  ergs. A calculation on the assumption that the valencies holding two atoms together are electrical leads to a value for the heat of dissociation equal to  $4.3 \times 10^{10}$  ergs. The author, therefore, concludes that chemical affinity is essentially of an electrical nature. J. W.

**The Hydrogenation of Closed Chains.** By F. STOHMANN and H. LANGBEIN (*J. pr. Chem.*, [2], 48, 447—453; compare Abstr., 1891, 376, 1146).—The following values are given (table, p. 81).

Inasmuch as these values are known for benzene and hexane, there is now a complete series of values for the hydrogenation of benzene. A comparison of them shows that the attachment of each pair of hydrogen atoms to the benzene molecule is not accompanied by the same thermal change. It must, therefore, be concluded that there are not three double bonds of equal value in the benzene ring. The bonds in benzene itself require a greater energy for their opening

	Heat of combustion of 1 gram molecule.		Heat of formation from elements
	Constant pressure.	Constant volume.	
Dihydrobenzene .....	848.0 Cal.	846.8 Cal.	- 8.0 Cal.
Tetrahydrobenzene ....	892.0 "	890.5 "	+ 17.0 "
Hexahydrobenzene ....	933.2 "	931.5 "	+ 44.8 "

up than those in any of the hydrogenated benzenes. The bonds in di- and tetra-hydrobenzene require less energy than those of either benzene or hexahydrobenzene, whilst those of the last-named compound require less than those of benzene.

A. G. B.

**State of Matter near the Critical Point.** By B. GALITZINE (*Ann. Phys. Chem.*, [2], 50, 521—544).—The author arrives at the following conclusions from his observations:—

The temperature of the actual appearance of the meniscus on cooling must lie considerably lower than the critical temperature, so that the optical method as usually carried out by observations of clouding in the tube must lead to erroneous values for the critical point.

If the cooling is conducted very slowly and regularly, there is no clouding.

The temperature at which the meniscus really appears, and the temperature at which the last traces of inhomogeneity vanish, must be regarded as independent of the quantity of substance in the tube.

The density  $\rho$  of a liquid in contact with its saturated vapour, and the density  $\varepsilon$  of this vapour, vary with the time at the same constant temperature, and also if they are heated several times beyond the critical point,  $\rho$  decreasing, and  $\varepsilon$  increasing. These two magnitudes, therefore, are not functions of the temperature alone.

At temperatures considerably higher than the critical point, a substance can have two different densities at almost the same pressure, the difference amounting to as much as 25 per cent.

J. W.

**Weight of a Litre of Normal Air: Densities of Gases.** By A. LEDUC (*Compt. rend.*, 117, 1072—1074).—The proportion by weight of oxygen in the air at Sorbonne was found to vary from 2.14 to 23.20 per cent., and since this variation would make a difference of 0.1 milligram in the weight of a litre of air, it is useless to attempt to reach a higher degree of accuracy in such determinations unless the composition of the air is determined at the same time.

The weight of a litre of average air at Paris at 0° and 760 mm. was found to be 1.29315 gram.

The author defines as *normal air* air collected on a plain in calm weather at some distance from a town, and containing a little more than 23.2 per cent. of oxygen by weight, or almost exactly 21.0 per cent. by volume. A litre of such air weighs 1.2932 grams at 0° and 760, and its mass is 1.2758 grams under 1 atmosphere c.g.s.

In accurate estimations of densities of gases it seems preferable to take nitrogen as the standard, since this gas is easily obtained in a state of purity, and its density is so near that of air that the presence of a small quantity of the latter in the apparatus introduces no appreciable error. The weight of a litre of nitrogen at Paris under normal conditions is 1.2570 grams, and its mass under a pressure of 1 atmosphere c.g.s. is 1.24006 grams, or better, 1.24 grams.

C. H. B.

**Critical Pressures in Homologous Series of Carbon Compounds.** By E. MATHIAS (*Compt. rend.*, 117, 1082—1085).—In the homologous series of the primary alcohols, the alkyl chlorides, the alkyl salts of formic, acetic, and propionic acids, the simple and mixed ethers, and the alkyl derivatives of ammonia, the critical pressures  $\pi$ , like the critical densities, are a continuous function of the total weight of the molecule, and, except in the case of the ammonia derivatives, it is possible to pass from one curve to the other by a simple linear substitution of the form  $\pi' = a\pi + \beta$ ;  $a$  and  $\beta$  being numerical constants which separately may be *nil*. Within the limits of the experimental errors, the curves of the critical pressures can be assimilated to arcs of equilateral hyperbolas, with asymptotes parallel with the axes of the coordinates, and can, therefore, be represented by the equation  $(\pi + a)(n + b) = c$ . In the case of the alcohols, and, therefore, in all the monosubstitution derivatives,  $b = 3$ .

By the method of substitution it is found that the critical pressure of hydrogen is 72.66 atmos., a value which is much higher than that obtained directly by Wroblewski, and which explains the difficulty of obtaining liquid hydrogen in a static condition.

The critical pressures of the alkyl salts derived from the primary alcohols are represented by the formula

$$\pi = \frac{1}{3}n' + 7.5 + \frac{600}{(n + 3)(n' + 4)},$$

where  $n'$  is the number of carbon atoms in the acid.

The critical densities  $\Delta$  and the critical pressures  $\pi$  in a given homologous series being continuous functions of the molecular weights, it follows that in each series there is a relation between  $\Delta$  and  $\pi$  which is independent of the particular compound considered.

C. H. B.

**Dissociation of Water.** By J. J. A. WILS (*Zeit. physikal. Chem.*, 12, 514—523).—In a former paper (*Abstr.*, 1893, ii, 364), the extent to which pure water may be regarded as dissociated electrolytically was calculated from the rate of hydrolysis of methylic acetate by water. The number then obtained was considered as being too low, owing to the fact that the acetic acid liberated in the reaction retards the hydrolysis during the first period, by the influence of its dissociated hydrogen ions on the hydroxyl ions of the water. In order to calculate and allow for this influence, fresh determinations of the rate of hydrolysis of methylic acetate by water have been made, the acetic acid liberated being determined by measuring the conductivity of the solution. From these results the concentration of the hydroxyl ions in water is calculated as  $0.14 \times 10^{-6}$ , but the author is somewhat

doubtful of the purity of the water used, and proposes to repeat the experiment under circumstances that will ensure greater accuracy.

H. C.

**Action of Salts on Acids.** By R. W. WOOD (*Amer. Chem. J.*, 15, 663—670).—Duggan's work on "absolute neutrality" (*Abstr.*, 1886, 765) cannot be considered conclusive, as the diastase used as an indicator was not sensitive enough. His view that the amylolytic function of that ferment is due to the presence of small traces of acid or alkali is not in accordance with his experimental results. It is more probable that the inhibition is due to free ions, of hydrogen in the case of acids, and of hydroxyl in the case of alkalis, "absolute neutrality" occurring only when these ions are formed at equal rates. The salts of "weak" acids in solution may be regarded as partly hydrolysed into the acids and bases; and as the latter split up more readily than the former, there is a tendency for normal salts to appear alkaline towards diastase.

The author prepares diastase directly from pale barley-malt by precipitating the cold aqueous extract with alcohol, and drying the washed precipitate in a vacuum over sulphuric acid. The ferment thus obtained is both powerful and sensitive; it is capable of hydrolysing 70 times its weight of starch, and the rate of hydrolysis is distinctly lowered by the addition of 1 part per million of sodium hydroxide (phenolphthalein is sensitive only to 8 parts per million).

The experiments were made on a uniform plan. The emulsion of starch (2 grams in 80 c.c. of water) was heated to 55° in a chamber surrounded by acetone vapour, the diastase (0.01 gram) added, and the mixture heated for 30 minutes. Aqueous soda (2 c.c. of 10 per cent.) was then added to inhibit the action of the diastase, and the reducing sugar formed estimated with alkaline copper tartrate.

The inhibitory effect of acids is less powerful than that of alkalis. In every case the initial action is to increase the activity; this is probably due to the presence of a trace of impurity in the starch. The action of the first five normal acids of the fatty series is much affected by temperature, the inhibitory power of the acids increasing faster than the hydrolytic power of the diastase.

Neutral salts of "weak" acids have a slight inhibitory action, as stated above, but those of "strong" acids are without action; in general, the "weaker" the acid the less the effect. The addition of free acid to normal salts first increases the inhibitory effect and then decreases it; but the variation is less marked than in the absence of the salt. At the maximum, the amount of acid may be varied between considerable limits without affecting the rate of hydrolysis. This is probably due to a want of sensitiveness even of the purer diastase; Duggan's results, therefore (*loc. cit.*), may readily be accounted for.

JN. W.

**Freezing Point of Dilute Solutions.** By H. C. JONES (*Zeit. physikal. Chem.*, 12, 623—656).—The author has determined the freezing points of the solutions of the following electrolytes between the limits of about 1/10 normal and 1/1000 normal:—Hydrochloric acid, sulphuric acid, nitric acid, phosphoric acid, potassium hydroxide, sodium hydroxide, ammonia, potassium carb-



onate, and sodium carbonate. In general the degree of dissociation calculated from the depression of the freezing point agrees fairly well with that calculated from the electric conductivity, being somewhat less in the case of the acids and bases, and affected by hydrolysis in the case of the carbonates.

The following organic compounds (practically non-electrolytes) were also investigated:—Cane sugar, glucose, carbamide, phenol, ethylic alcohol, propylic alcohol. The depression constant obtained for the most dilute solutions of these substances is much greater than the calculated constant for water. With increasing concentration, the molecular depression sinks to a minimum, and then either remains constant, or again increases, as in the case of the two carbohydrates. With phenol, the minimum was apparently not reached.

For the feeble conductors acetic acid and succinic acid, there is an approximate agreement between the values of the dissociation ratio calculated from the freezing point depression and from the electrical conductivity.

The depression constants obtained for water from solutions of carbamide, ethylic alcohol, and propylic alcohol were 1·888, 1·876, and 1·878 respectively, the value calculated from the latent heat of fusion (19·7), by means of Van't Hoff's formula, being 1·87. J. W.

**Rate of Crystallisation of Supercooled Liquids.** By B. MOORE (*Zeit. physikal. Chem.*, 12, 545—554).—A U-tube, open at both ends, was filled with a liquid (for example, acetic acid), and kept at a constant temperature below the freezing point of the latter. Crystallisation of the overcooled liquid was then induced in one limb, and the time taken for the boundary between the solid and liquid to pass downwards from one mark to another on that limb was noted. This time was found to be independent of the width of the tube, and approximately inversely proportional to the degree of overcooling. Experiments were made with phenol containing various proportions of water, in order to ascertain if the rate of crystallisation remained the same for the same degree of overcooling of the different mixtures. This was found not to be the case, the velocity in the mixture increasing at a much smaller rate with the degree of overcooling than when phenol alone was used. Cresol mixed with phenol greatly diminished the rate of crystallisation. J. W.

**Solubility of Mixed Crystals.** By A. FOCK (*Zeit. physikal. Chem.*, 12, 657—662).—The isomorphous double salts  $2\text{KCl}, \text{CuCl}_2, 2\text{H}_2\text{O}$  and  $2\text{NH}_4\text{Cl}, \text{CuCl}_2, 2\text{H}_2\text{O}$  were mixed in various proportions, dissolved in water, and the solutions allowed to crystallise by spontaneous evaporation at 17°. As soon as a quantity of mixed crystals sufficient for analysis had separated, they were removed and analysed along with a sample of the solution taken at the same time. The solutions always contained a larger proportion of the salt  $2\text{KCl}, \text{CuCl}_2, 2\text{H}_2\text{O}$  than the mixed crystals, and as evaporation proceeded, proportionately more and more ammonium salt was removed from the solution. The series of mixtures, however, is not continuous, crystals containing 27·77 and 54·87 molecules of  $2\text{KCl}, \text{CuCl}_2, 2\text{H}_2\text{O}$  per cent. respectively forming the

limits at the temperature observed. The replacement of ammonium by potassium in the solution appears to cease when these limiting crystals exist together in contact with the solution, the composition of the solution remaining constant until all the crystals of 27.77 per cent. have been removed, or transformed into those of 54.87 per cent.

When solutions of ammonium sulphate and potassium sulphate were allowed to crystallise together, it was found that the molecular percentage of ammonium sulphate in the mixed crystals was very nearly proportional to the concentration of the solution with respect to ammonium sulphate. J. W.

**Isomorphism. Part VIII.** By J. W. RETGERS (*Zeit. physikal. Chem.*, 12, 583—622; compare *Abstr.* 1891, 146, and 1151; *Abstr.* 1892, 1048; *Abstr.*, 1893, ii, 161).—Schröder van der Kolk (*Abstr.*, 1893, ii, 280) suggested that the ferric chloride contained in Scheele's ruby-coloured ammonium chloride crystals might be in the form of an isomorphous admixture of the regular hydrate of ferric chloride described by him. The author rejects this suggestion on the ground that the regular hydrate of ferric chloride is colourless, and could not produce the intense colour of the mixed crystals. He is of opinion that isomorphism in this case is altogether excluded, and that the most satisfactory explanation is that the ferric chloride is merely an enclosed hydrate, probably  $\text{Fe}_2\text{Cl}_6 \cdot 7\text{H}_2\text{O}$ . The regular crystals he considers to be most probably an unstable form of a hydrate with much more water than the yellow hydrate,  $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ .

When sulphur and selenium crystallise together from their solution in methylenic iodide, the sulphur crystals are coloured yellowish-brown by admixture of selenium. No such mixed crystals are formed when sulphur and tellurium are crystallised simultaneously from warm methylenic iodide. The sulphur crystals in this case are pale yellow, and crystallise out quite independently of the opaque, metallic tellurium which separates beside them. The author considers that this shows that whilst sulphur and selenium are isodimorphous, sulphur and tellurium are not.

From an extensive series of experiments on the crystallisation of salts from aqueous solutions strongly coloured by organic dyes, the author finds that in almost all cases colourless crystals separate. The exceptions are strontium nitrate, which is coloured by vegetable dyes, as observed by Sénarmont; potassium sulphate, which is coloured by Bismarck-brown; potassium nitrate, which is coloured by nigrosin; ammonium nitrate, which is coloured by indulin; and barium chloride, which is coloured by "Wasserblau." Sénarmont's speculation that salts with much water of crystallisation would show the property of absorbing colouring matters was not confirmed, most of the above-mentioned salts being anhydrous, and no coloration taking place with such strongly hydrated salts as Glauber's salt, alum, sodium thiosulphate, and sodium phosphate.

J. W.

**Endothermic Reactions effected by Mechanical Force.** By M. C. LEA (*Amer. J. Sci.*, [3], 46, 241—244).—In a former paper

(Abstr., 1893, ii, 69), the author showed that silver haloïds may be decomposed by the application of a high pressure, and he has been thus led to examine whether the same agent, mechanical force, would not be capable of bringing about analogous chemical changes in other compounds. Pressure was applied as before by means of a combination of screw and lever, the calculated maximum pressure obtainable without allowing for loss by friction being over a million pounds per square inch. The material was wrapped in either platinum or silver, usually platinum, foil. There was no action in any case on the metal, which preserved its full brightness in the parts in contact with the material, so that the effects observed were due to pressure only.

Silver sulphite in platinum foil was moderately darkened by two days pressure. Silver salicylate was rendered very dark by two days pressure. Silver carbonate was moderately darkened by a somewhat longer pressure. Silver tartrate and silver oxide were not affected.

Ferric oxide, recently precipitated and dried, was unaffected by pressure, no ferrous oxide being formed.

Potassium Platinobromide.—Where the pressure was greatest the brilliant red colour of this substance was blackened, not superficially only, but all through. Ammonium platinobromide showed moderate but well marked darkening.

Potassium Chlorate.—When this substance was subjected to pressure by itself, no effect whatever was produced, and not a trace of chloride was formed. But when it was mixed with silver nitrate, both in fine powder, and subjected to pressure, there was an evident formation of silver chloride. The material was no longer completely soluble in water, but left an abundance of white flakes which darkened when exposed to light.

Mercuric oxide darkens slightly but very distinctly, and this change seems to be accompanied by a slight loss of weight, requiring, however, very careful weighing to detect it. The darkened part, as well as the rest, dissolves without difficulty in acetic acid, and consisted, therefore, probably of traces of mercurous oxide and not of metallic mercury. Mercurous chloride and mercuric chloride remained unchanged. Mercuric iodide darkened considerably, and at points where the pressure was greatest, it became absolutely black. It did not appear, however, that any iodine was set free; none could be extracted with alcohol. With mercuric oxychloride,  $2\text{HgO}, \text{HgCl}_2$ , heavy pressure caused much darkening.

Sodium thiosulphate compresses to a hard, translucent cake, but does not decompose.

Although in all these instances the darkening is well marked, the actual proportion of material affected is small, so that in many cases it is difficult to apply tests to decide as to the precise nature of the substances formed. In some cases, however, this can be done, and the author concludes that many of the salts of easily reducible metals, especially of silver, mercury, and platinum, undergo reduction by pressure. Such reactions are endothermic, and it therefore follows that mechanical force can bring about reactions which require expenditure of energy, which energy is supplied by mechanical force

in the same way that light, heat, and electricity supply energy in the endothermic changes which they bring about. H. C.

*Note by Abstractor.*—Formation of allotropic modifications, at any rate in the case of the mercuric compounds, appears possible.

H. C.

**The Diamond as the Standard for the Determination of Atomic Weights.** By G. HENRICHS (*Compt. rend.*, 117, 1075—1078).—The author proposes that the diamond should be adopted as the standard matter for the determination of atomic weights. It is solid, compact, non-absorptive, and sufficiently hard to resist the mechanical effects of the necessary manipulations, and its resistance to the action of energetic chemical reagents makes the removal of impurities comparatively easy. Moreover, its purity is unquestionable, and it is not liable to contain mechanical inclusions. Oxygen has almost invariably to be determined by difference, whilst hydrogen is probably the worst standard that could be selected, owing to its low atomic weight, the difficulties of manipulation, and the difficulty of obtaining it pure.

If  $C = 12$ , it follows from the determinations of Dumas, Erdmann, Marchand, and Roscoe that  $O = 16$ , and from the determination of Erdmann and Marchand, that  $Ca = 40$ .

The mutual dependence of all the atomic weights can be represented by means of a parabola, with diamond at the vertex and calcium at the focus, the primary elements being placed on the curve at the proper distance from the vertical passing through the zero of the atomic weights. The secondary axis passing through this point will be the locus of the atomic weights determined indirectly. Adopting recognised experimental results, it appears that, with very small errors,  $P = 31$ ,  $Fe = 56$ ,  $Zn = 65.5$ ,  $Cd = 112$ ,  $Hg = 200$ ,  $Pb = 207$ , and  $H = 1.0$ ,  $Mg = 24$ ,  $S = 32$ ,  $Be = 9$ ,  $Cu = 63.5$ , and  $F = 19$ . For the proper determination of the atomic weights of the halogens, a revision of the atomic weight of silver is necessary, and this element might then serve as a secondary standard.

C. H. B.

**Beckmann's Method for determining Molecular Weights.** By G. BARONI (*Gazzetta*, 23, ii, 249—291; compare *Abstr.*, 1893, ii, 511).—The small variations in the barometric height which often occur during the determination of molecular weights by Beckmann's method have a considerable influence on the accuracy of the result; they are, therefore, not negligible, as is usually supposed. The error introduced by variations in the atmospheric pressure during the determination may amount to one-half the molecular weight of the substance. The author has determined the molecular weight of sodium bromide, strontium and mercuric chlorides, potassium and silver nitrates, potassium sulphate, chromate, and dichromate, iodic, succinic, oxalic, tartaric, and citric acids, mannitol, and cane sugar in aqueous solution, and of phenol and resorcinol, using benzene as the solvent. The curves plotted with the concentrations as abscissæ and the molecular weights as ordinates rise, in the majority of cases, in accordance with the requirements of the dissociation hypothesis.

The curves obtained for potassium chromate, bromide, and chloride, and for citric acid, first rise and then fall; in the cases of barium, sodium, and strontium chlorides, sodium bromide, and tartaric acid, the curves fall throughout the whole length examined. The cause of this behaviour is unknown. W. J. P.

**Graphochemistry of Oxides and their Combinations.** By E. NICKEL (*Zeit. physikal. Chem.*, 12, 663—669).—The author has applied his graphochemical method (compare Abstr., 1892, 1158) to the tabulation of the oxides with respect to their composition, properties, and combinations with each other. To obtain a table for their composition, he makes use of the following considerations. If  $E$  is the symbol of an element, each oxide may be expressed as  $EO_n$ , and if  $p$  be the atomic weight of the element and  $x$  the percentage of oxygen in the oxide, then  $p/16n = (100 - x)/x$ . The table is constructed by taking the values of  $p$  and  $n$  (or  $16n$ ) as ordinates and abscissæ respectively,  $x$  then appearing as a bundle of rays diverging from the origin. All the oxides of each element are found in a horizontal line, and all the oxides with the same atomic oxygen ratio in the same vertical line. If the elements are gone through in the order of their atomic weights, a curve like Lothar Meyer's spiral is obtained when the typical oxides are considered. J. W.

## Inorganic Chemistry.

**Molecular Weight of Hydrogen Peroxide.** By G. TAMMANN (*Zeit. physikal. Chem.*, 12, 431—432).—A redetermination of the molecular weight of hydrogen peroxide by the cryoscopic method gives the molecular formula  $H_2O_2$ , in place of  $H_2O_4$ , as formerly given by the author (Abstr., 1890, 106), and accords, therefore, with the results of Carrara's determination (Abstr., 1893, ii, 163).

H. C.

**Occurrence of Hydrogen Peroxide in the Atmosphere and in Atmospheric Discharges.** By E. SCHÖNE (*Ber.*, 26, 3011—3027).—During 1874–75 the author carried out systematic observations of the atmosphere in the neighbourhood of Moscow, and was led to affirm the presence in it of hydrogen peroxide. This conclusion was questioned by L. Ilosvay in 1889, whose arguments may be thus summarised. 1. The reactions with potassium iodide, starch, ferrous sulphate, guaiacum tincture, and malt extract are not characteristic of hydrogen peroxide, and may also be produced by nitrous acid. 2. Characteristic reagents fail to show the presence of hydrogen peroxide in the atmosphere. 3. No chemical process is known by which hydrogen peroxide and ozone are produced in nature. 4. Ozone is not formed during rapid combustion, and hydrogen peroxide only in circumstances which prevent its passing into the atmosphere. 5. The

negative results obtained from certain special experiments designed to show the presence of hydrogen peroxide. The author criticises and refutes these conclusions in detail. 1. Ilosvay's statements about the reagents are partly due to errors of manipulation and partly to lack of precautions in the preparation of the various solutions. 2. Titanic acid, which is stated to be the only characteristic reagent for hydrogen peroxide, is capable of detecting not less than 1 : 90,000, but in only two cases out of 500 has the author found more than 1 : 1,000,000. 3. Apart from electrical discharges, the author suggests that the action of sunlight, air, and moisture on ethereal oils and similar substances would result in the production of ozone and of hydrogen peroxide. 4. The formation of hydrogen peroxide during combustion has been proved by the independent observations of several chemists by more exact methods than Ilosvay's. 5. The results of Ilosvay's crucial experiments are invalid for the following reasons. (a) The air was taken from the streets of Budapest; (b) the volume (171—500 lit.) was far too small; (c) as hydrogen peroxide is unstable in presence of alkalis, the soda employed to absorb it would cause its decomposition during the long continuance (2—5 weeks) of the experiments; (d) the passage of the air through the various purifying solutions (soda and dilute sulphuric acid) would cause the complete absorption of hydrogen peroxide, and consequently account for the various reagents such as thallium paper and azobenzene-naphthylamine being unaffected. Samples of rain water, tested during the past two years, show that there is no connection between the quantities of hydrogen peroxide and nitrites which they contain.

J. B. T.

**Manufacture of Oxygen from Calcium Plumbate.** By G. KASNER (*Chem. Zeit.*, 17, 1242).—In investigating the dissociation of calcium plumbate, H. Le Chatelier (*Abstr.*, 1893, ii, 524) found that for the evolution of oxygen by heat alone it is necessary to raise temperature about 200° higher than in the case of barium peroxide; on the other hand, at lower temperatures the oxygen is more quickly and completely reabsorbed from air by the plumbate than by the barium oxide. The author now calls attention to the fact that whilst in his earlier communications he mentioned the evolution of oxygen from calcium plumbate by heat alone, he recommended, as more generally useful, several other methods; the following is especially advantageous. Porous calcium plumbate is moistened with steam and subjected to the action of washed furnace gases, preferably, at a temperature below 100°. The carbonic anhydride of the furnace gases is rapidly absorbed, and the material, which retains its porous condition, then consists of a mixture of calcium carbonate and lead peroxide. This is transferred to a retort kept constantly at a red heat, and in this the oxygen is evolved, the evolution being much helped by the introduction of a current of steam. After the evolution of the oxygen, the current of steam is continued, and the temperature raised, when carbonic anhydride is liberated, and may be collected for use. The calcium plumbate is then regenerated by means of a current of air. The author also refers to Peitz's patented

modification, in which it is proposed to decompose the plumbate by means of a current of pure carbonic anhydride at a red heat.

The author claims for his plumbate process, as advantages over the Brin barium oxide process, (a) obtaining pure carbonic anhydride as a bye-product; (b) the use of low temperatures, and consequent saving in fuel and in wear and tear of retorts. (See also Abstr., 1891, 392.)  
L. T. T.

**Molecular Weight of Persulphates and Permolybdates.** By G. MUELLER (*Zeit. physikal. Chem.*, 12, 555—563).—The molecular weights of potassium persulphate and of ammonium persulphate were found by the author, from a consideration of the electrical conductivity and the cryoscopic behaviour of their solutions, to be in correspondence with the formulæ  $K_2S_2O_8$  and  $(NH_4)_2S_2O_8$  (compare Bredig, Abstr., 1893, ii, 572).

The conductivity and freezing point depressions of Péchard's potassium permolybdate and ammonium permolybdate point to these substances having the formulæ  $K_2Mo_2O_8$  and  $(NH_4)_2Mo_2O_8$  respectively.  
J. W.

**Action of Nitric Peroxide on Metals and Metallic Oxides.** By P. SABATIER and J. B. SENDERENS (*Bull. Soc. Chim.*, [3], 9, 668—669; compare Abstr., 1892, 1390).—Brown tungstic dioxide becomes incandescent in nitric peroxide at 300°, and yields yellow tungstic anhydride mixed with a little blue oxide,  $W_2O_5$ .

Sodium is not oxidised by nitric peroxide in the cold, and is but slowly attacked on heating. Reduced nickel ignites at the ordinary temperature, and forms nickelous oxide.  
W. T.

**A New Sulphide of Carbon.** By B. v. LENGTEL (*Ber.*, 26, 2960—2968).—When pure, dry carbon bisulphide is boiled in a reflux apparatus, the vapour being exposed to an electric arc maintained between two carbon poles for two or three hours, the interior of the apparatus becomes blackened, and a black substance is found suspended in the liquid. If this is filtered off, a cherry-red liquid is obtained, which has a remarkably strong odour, and produces great irritation of the eyes. This liquid is allowed to stand for 6—8 days over metallic copper to remove free sulphur, and is then evaporated by means of a current of dry air. A deep red liquid is thus left which has the composition of a *tricarbon bisulphide*,  $C_3S_2$ . It evaporates in the air very slowly, and its vapour has a most vigorous action on the mucous membrane, a very small trace causing violent catarrh. Placed on the skin, it merely produces a black spot. The sp. gr. of the liquid is 1.27369. When heated, it is converted into a hard, black mass of almost the same percentage composition, which is probably a polymeride. When the liquid is rapidly heated to 100—120°, this change takes place with explosive violence, but occurs gradually when it is gently warmed. The same substance is formed when the liquid is preserved for a few weeks, and its formation is in all cases accompanied by the production of a little carbon bisulphide. The liquid can be distilled under diminished pressure at 60—70°, but

a portion of it is always converted into the solid modification. The liquid substance is insoluble in water, in which it sinks, but is readily soluble in alcohol, ether, chloroform, benzene, and carbon bisulphide. From a concentrated solution in the solvent last mentioned, the solid modification is deposited, but a dilute solution is more stable. It burns with a luminous, smoky flame, carbonic and sulphurous anhydrides being formed. Aqueous potash and soda give almost black solutions, in which acids produce black precipitates, whilst alcoholic potash acts vigorously and yields a deep brown solution. A drop of concentrated sulphuric acid causes violent hissing, and the whole mass is converted into the solid modification. Concentrated nitric acid causes ignition, whilst a more dilute acid dissolves the liquid, neither carbonic anhydride nor sulphuric acid being formed.

The analyses of the liquid show rather less carbon, those of the solid rather more, than that required by the formula  $C_3S_2$ . A determination of the molecular weight from the freezing point of the solution in benzene gave numbers which agree well with the formula.

The solid modification is hard, has a fine, granular fracture, and is insoluble in water and all ordinary solvents. Aqueous potash dissolves it completely, and it appears to be precipitated unaltered on the addition of an acid. When heated, it decomposes, with formation of sulphur, which sublimes, and a gas which contains sulphur, but is not carbon bisulphide, and is being further investigated.

When bromine is added to a solution of the liquid tricarbon disulphide in chloroform, heat is evolved, and a yellow precipitate produced; this has the composition  $C_3S_2Br_2$ , has an aromatic odour, and is insoluble, or only very slightly soluble, in all solvents. Under similar conditions, a yellow precipitate is produced with chlorine, but not with iodine.

The author is investigating the structure of this bromide.

A. H.

**Preparation of Metallic Lithium.** By GUNTZ (*Compt. rend.*, 117, 732—733).—In the preparation of lithium, the yield is higher the lower the temperature at which electrolysis takes place. Lithium chloride melts at  $600^\circ$ , a mixture of equal weights of lithium and potassium chlorides melts at about  $450^\circ$ , and a mixture of the two chlorides in molecular proportion at about  $380^\circ$ ; a mixture of 2 mols. of potassium chloride with 1 mol. of lithium chloride melts at about  $550^\circ$ , and potassium chloride alone at  $740^\circ$ .

The best mixture for electrolysis contains equal weights of the two chlorides, for then the melting point of the saline mixture falls as decomposition proceeds. The negative electrode should be a rod of carbon about 8 mm. in diameter, and the positive electrode a rod of iron 3 to 4 mm. in diameter, surrounded by a glass tube about 20 mm. in diameter. A current of 20 volts and 90 ampères is necessary, and the metal obtained contains from 1 to 2 per cent. of potassium.

It would seem that when electrolysis takes place at a red heat, the lithium at the negative electrode combines with the lithium chloride to form a subchloride,  $Li_2Cl$ , which has a higher resistance than the original chloride, and thus reduces the intensity of the current. The



subchloride diffuses through the liquid and combines with chlorine at the positive electrode. At  $500^{\circ}$ , or below, it would seem that this formation of subchloride does not take place. C. H. B.

**Calcium Oxyiodide.** By TASSILLY (*Bull. Soc. Chim.*, [3], 9, 629—630).—Calcium oxyiodide,  $\text{CaI}_2 \cdot 3\text{CaO} + 16\text{H}_2\text{O}$ , has been obtained in needles, sometimes 2 cm. long, by heating quicklime with a concentrated solution of calcium iodide in a sealed tube at  $150^{\circ}$  for six hours. It is also formed by the addition of quicklime in small portions to a boiling concentrated solution of calcium iodide. Long needles are obtained on cooling this solution, which cannot be freed from adhering lime. W. T.

**Double Salts of Potassium and Magnesium Sulphate: Schönite and Potassium Astrachanite.** By J. K. VAN DER HEIDE (*Zeit. physikal. Chem.*, 12, 416—430).—The author has already recorded the formation of potassium astrachanite,  $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ , from a solution of schönite,  $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  (Abstr., 1893, ii, 276), and in order to obtain further data respecting the conditions under which it is produced, has now examined the behaviour of the sulphates of potassium and magnesium towards one another in solution at all possible temperatures. The following are the principal facts resulting from this investigation.

1. Temperature,  $-4.5^{\circ}$ . Formation from ice and the two sulphates of the saturated solution of the latter.

2. Temperature,  $-3^{\circ}$ . Formation of schönite from the two sulphates

3. Temperature,  $47.2^{\circ}$ .  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , changes in the presence of schönite into  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ .

4. Temperature,  $72^{\circ}$ . Potassium astrachanite is formed from schönite in the presence of  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ .

5. Temperature,  $92^{\circ}$ . Potassium astrachanite is formed from schönite in the presence of  $\text{K}_2\text{SO}_4$ .

6a. Temperature,  $102^{\circ}$ . Boiling point of the saturated solution of potassium astrachanite and sulphate.

6b. Temperature,  $103^{\circ}$ . Boiling point of the saturated solution of potassium astrachanite and  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ .

7. Temperature,  $106^{\circ}$ . Formation of kieserite in the presence of potassium astrachanite. H. C.

**Modifications of Silver.** By H. LÜDTKE (*Ann. Phys. Chem.*, [2], 50, 678—695).—The silver of deposited silver mirrors has properties different from those of ordinary silver, and the author has investigated these electrically with the following results.

Lehmann's assumption that a thin layer of sodium silicate on all glass surfaces has something to do electrolytically with the deposition of silver, must be incorrect, for silver mirrors may be deposited on mica, porcelain, quartz, Iceland spar, platinum, &c.

The electrical resistance of several sorts of silver mirrors decreases considerably as time elapses. There is no such decrease in the case of mirrors reduced by milk sugar or by Martin's method.

The allotropic mirror silver may easily be converted into ordinary silver by heat, light, chemical reagents, &c.

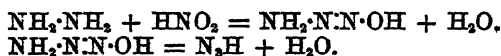
The mirror silver and other allotropic preparations show an initial difference of potential of about 0.1 volt against ordinary silver in dilute acids, the allotropic modification being the positive pole. The difference is smaller in silver nitrate solution, and the ordinary silver is then the positive pole.

All the properties of mirror silver indicate that in its original modification it is identical with solid colloidal silver.

The black silver sponge obtained by reducing silver nitrate solution with zinc passes into a grey modification on contact with acids. This transformation is accompanied by an increase in the electric conductivity.

J. W.

**Method of Formation of Silver Nitride.** By A. ANGELI (*Gazzetta*, 23, ii, 292—294).—On adding a saturated hydrazine sulphate solution to a cold saturated solution of silver nitrite, the liquid immediately becomes turbid, and silver nitride separates in white needles. The reaction probably proceeds in accordance with the following equations.



This simple method of preparing the salt forms a very striking lecture experiment, and may be very rapidly performed.

W. J. P.

**Preparation of Cuprous Oxide.** By E. J. RUSSELL (*Chem. News*, 66, 308).—A fairly concentrated solution of copper sulphate along with excess of sodium chloride is thoroughly reduced by treatment with gaseous sulphurous anhydride, the excess of the latter is then expelled by heating, and solid sodium carbonate is added to the hot solution; bright red cuprous oxide is precipitated and is readily washed by decantation.

D. A. L.

**Stability of Dilute Solutions of Mercuric Chloride.** By L. VIGNON (*Compt. rend.*, 117, 793—795).—Aqueous solutions containing 0.1 per cent. of mercuric chloride gradually deposit a white precipitate if exposed to the air, but remain practically unchanged for many days in well closed vessels. In presence of magenta or indigo-carmin the quantity of precipitate formed in a given time is reduced, and in this respect indigo-carmin is a better preservative than magenta. In presence of 0.1 per cent. of hydrochloric acid of 22°, or of 1 per cent. of sodium, ammonium, or potassium chloride, the solution remains practically unchanged for a much longer time.

C. H. B.

**Stability of Mercuric Chloride Solutions.** By TANBET (*Compt. rend.*, 117, 1081—1082).—The formation of a white precipitate in dilute solutions of mercuric chloride (preceding abstract) is due to the presence of ammonia in the atmosphere, and does not take place with pure air even when large quantities of the latter are passed through the liquid.

C. H. B.

**Action of Mercurous Chloride on Silver Chloride in presence of Ammonia.** By U. ANTONY and G. TURI (*Gazzetta*, 23, ii, 231—237).—Pesci (Abstr., 1892, 685) has shown that the black precipitate obtained by treating mercurous chloride with ammonia contains metallic mercury; this observation explains the well-known fact that, on adding ammonia to the white precipitate obtained with hydrochloric acid in a mixed solution of silver and mercurous salts, silver is retained in the black precipitate. If the precipitate remains long in contact with ammonia, the reaction represented by the following equation may occur:—



On repeatedly washing the mixture of silver chloride and mercurous chloride with ammonia solution on a filter, a residue was ultimately obtained which contained 1.16 per cent. of silver, instead of 30 per cent. as indicated by the above equation. When, however, the mixed chlorides precipitated from a solution containing excess of silver salt were digested with ammonia for some time, the resulting precipitate was found to contain the quantity of silver indicated by the equation. During a qualitative analysis, therefore, if silver is not found in the filtrate from this black precipitate, the latter should be examined for the metal.

W. J. P.

**Sublimation of Red and Yellow Mercuric Iodides.** By BERTHELOT (*Compt. rend.*, 117, 827—828).—The author confirms Frankenheim's statement that when a mixture of red and yellow mercuric iodides is carefully heated on a glass plate and allowed to condense on another plate held at a short distance above it, the sublimate is a mixture of the red and yellow iodides. The result, however, cannot be regarded as proof of the existence of the red iodide in the state of vapour. There is little doubt that solid particles of the red iodide are mechanically projected from the lower plate to the upper, and bring about the immediate conversion of the yellow iodide that condenses in contact with them.

C. H. B.

**Action of Water on Glass.** By F. KOHLRATSCH (*Ber.*, 26, 2998—3003).—Analyses have been made of the substances extracted by water at ordinary temperatures from finely powdered glass of various kinds. A comparison of the soluble portion with the original glass shows that, in the former, the relative quantity of alkali increases and that of the silica diminishes; in one case, the solution contained three times as much alkali and half as much silica as the original glass, which was rich in alkali. With Bohemian potash glass (rich in silica), the discrepancy was less. Both of these glasses are largely employed in the manufacture of chemical apparatus. At present, it is impossible to decide whether the solution of the alkali precedes and causes that of the silica, but the author's experiments show that practically they dissolve simultaneously.

A sample of Jena "apparatus" glass and two of a glass free from alkali were examined in a similar manner, and, after two months' treatment with water, the solutions contained 72, 85, and 57 milli-

grams per litre respectively. A flask of the Jena glass, after two days at ordinary temperatures, lost 0.005 milligram, after 200 days 0.066 milligram, after 24 hours at  $94^{\circ}$ , 0.8 milligram per sq. dm. Experiments were also conducted to show the relative insulating power of different sorts of glass under varying conditions of atmospheric moisture; glass of poor quality conducts after exposure for a few seconds in presence of 40–50 per cent. of moisture, whilst the glass free from alkali insulates well in presence of 80 per cent. The composition of the alkali-free glass, in equivalents per cent., is as follows:— $\text{BaO} = 12$ ,  $\text{ZnO} = 3.7\text{--}4.6$ ,  $\text{Al}_2\text{O}_3 = 3.3\text{--}3.7$ ,  $\text{B}_2\text{O}_3 = 13\text{--}15$ ,  $\text{SiO}_2 = 65\text{--}68$ . J. B. T.

**Nitro-metals.** By P. SABATIER and J. B. SENDRENS (*Bull. Soc. Chim.*, [3], 9, 669–674; compare Abstr., 1892, 1390; 1893, ii, 374).

—**Nitro-cobalt.**—This substance is best prepared from cobalt reduced at a low temperature. Nitrogen peroxide, suitably diluted with nitrogen, is passed over the reduced metal in the reduction tube, when black nitro-cobalt,  $\text{Co}_2\text{NO}_2$ , is formed. Water acts on nitro-cobalt very vigorously, but gives less nitric oxide than with nitro-copper. A solution of cobalt nitrate containing very little nitrite is produced, with, sometimes, a precipitate of bluish-green, insoluble basic nitrite mixed with cobalt. Heated in a current of nitrogen, nitrous fumes are first evolved, and then decomposition takes place with almost explosive violence, a residue of metallic cobalt and oxide being formed. Nitro-cobalt explodes when mixed with combustible matter.

**Nitro-nickel.**—This compound resembles the cobalt compound in method of formation and properties; it has always been obtained mixed with oxide. It appears to give no special reaction with carbonic oxide.

**Nitro iron.**—This substance is much more difficult to prepare. Some nitric peroxide is first absorbed, and then deflagration takes place, even in a much diluted atmosphere of nitric peroxide.

W. T.

**Chromium Sulphates and Double Sulphates.** By T. KLORs (*Bull. Soc. Chim.*, [3], 9, 663–668).—The double sulphate,  $\text{Cr}_2(\text{SO}_4)_3 \cdot 3(\text{NH}_4)_2\text{SO}_4$ , has been prepared by adding chromic oxide to a large excess of ammonium sulphate kept in a state of quiet fusion. In this case, a clear, green, crystalline powder is obtained, whilst if violet ammonium chromium alum is substituted for the oxide, a pulverulent powder is obtained not so readily washed. It forms needles, 0.05 mm. long, and short spindles. The crystals are but slightly attacked by boiling water, not acted on by a concentrated solution of ammonium sulphate, and completely decomposed by boiling potash. Boiling concentrated sulphuric acid gives Traube's red sulphate. The salt is not decomposed by heating at  $350^{\circ}$  on a lead bath, but takes a transient violet colour. By calcination, it yields a very adherent, light oxide.

The double sulphate,  $\text{Cr}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4$ , is formed if the preceding preparation be heated so far as to volatilise most of the ammonium sulphate. It forms tabular, hexagonal crystals, which are more stable

than the needles described above, as they are not attacked by boiling water or concentrated hydrochloric acid; boiling potash (sp. gr. 1.3) acts on them but very slowly. Heat and concentrated sulphuric acid have the same action as on the needles.

These double sulphates correspond with the ferric ammonium sulphates obtained by Lachaud and Lepierre. They may be viewed as derivatives of Recoura's chromosulphuric acid,  $\text{H}_2\text{Cr}_2(\text{SO}_4)_4$ , and chromotrisulphuric acid,  $\text{H}_2\text{Cr}_2(\text{SO}_4)_3$  (Abstr., 1893, ii, 470).

Attempts to prepare the corresponding potassium and sodium salts failed, as the chromosulphates could not be obtained free from ammonia; potassium chromotrisulphate is obtained by fusing potassium chromium alum with excess of ammonium sulphate and potassium sulphate.

The red sulphate of chromium, referred to above, prepared in three different ways, has the formula  $\text{Cr}_2(\text{SO}_4)_3$ , and is, therefore, a normal salt. It is a powder, rose-coloured in daylight, but appears green by gas-light.

W. T.

**Complex Acids derived from Molybdic acid and Titanic and Zirconic acids.** By E. PÉCHARD (*Compt. rend.*, 117, 788—790).—When hydrofluosilicic acid is added to a warm solution of ordinary ammonium molybdate, the latter becomes yellow, and, on cooling, deposits a crystalline precipitate, if the solution is not too dilute. If hydrochloric acid is added to a dilute solution even, there is an immediate precipitation of the silicomolybdate,



described by Parmentier. Part of the molybdate is converted, at the same time, into oxyfluormolybdate.

Ammonium silicofluoride can be substituted for hydrofluosilicic acid, and a precisely similar method yields titanomolybdates and zirconomolybdates.

*Ammonium titanomolybdate*,  $2(\text{NH}_4)_2\text{O} \cdot \text{TiO}_2 \cdot 12\text{MoO}_3 + 10\text{H}_2\text{O}$ , is obtained by adding ammonium titanofluoride solution to ammonium molybdate solution until the intensity of the yellow colour no longer increases, and then adding hydrochloric acid. It is completely insoluble in solutions of ammonium salts, but dissolves in water and in acids, and crystallises in small, yellow octahedra, which act strongly on polarised light.

*Potassium titanomolybdate*,  $2\text{K}_2\text{O} \cdot \text{TiO}_2 \cdot 12\text{MoO}_3 + 16\text{H}_2\text{O}$ , is an efflorescent salt, obtained in yellow prisms by adding potassium chloride to a hot concentrated solution of the preceding compound and allowing the liquid to cool.

*Titanomolybdic acid*,  $\text{TiO}_2 \cdot 12\text{MoO}_3 \cdot 22\text{H}_2\text{O}$ , crystallises in golden-yellow octahedra, melting at about  $60^\circ$ , and very soluble in water. It is obtained by adding hydrochloric acid to mercurous titanomolybdate, which is prepared from one of the preceding salts by double decomposition. A more rapid method is to agitate with ether an aqueous solution of the ammonium salt acidified with hydrochloric acid and allow the heavy ethereal solution to evaporate spontaneously.

*Zirconomolybdates* are obtained in a similar way and are strictly

analogous in composition. The ammonium salt crystallises with  $10\text{H}_2\text{O}$  in yellow octahedra, and the potassium salt with  $18\text{H}_2\text{O}$  in efflorescent, yellow prisms. C. H. B.

**Action of some Metals on Acid Solutions of their Chlorides.** By A. DITTE and R. METZNER (*Compt. rend.*, 117, 691—694).—When a bar of tin is placed in a vessel containing a concentrated solution of stannous chloride in hydrochloric acid, on the top of which is a layer of water, crystals of tin rapidly form on the bar in the neighbourhood of the surface of separation of the two liquids. The system, as thus arranged, clearly consists of two identical electrodes immersed in two different liquids, and the two sources of electromotive force are the action of the acid on the tin and the diffusion of the acid into the supernatant water. If a bar of tin is placed simply in a hydrochloric acid solution of stannous chloride, no crystals are formed; if a thin layer of water is poured on the solution, it mixes with the subjacent liquid and becomes a conductor; if the layer of water is deep, it has its highest conductivity at the surface of separation, and the conductivity decreases gradually in a vertical direction as the upper surface of the water is approached. and, since the current traversing successive layers of the liquid diminishes in a similar manner, the size of the tin crystals shows corresponding variations, the deposit changing from well-defined crystals to a spongy, grey mass, and, finally, in the highest layers, to a very finely divided black powder.

Above the surface of separation, the bar of tin merely plays the part of the negative electrode, and can be replaced by any other conductor without any alteration in the phenomena. If, on the other hand, the metal rod or bar consists of two parts separated by some insulating material, and the latter lies on the surface of separation, no formation of crystals takes place until, by the progress of diffusion, the upper and lower parts of the rod are put into communication by two conducting liquids of different composition. The formation of the crystals is dependent on the action of the hydrochloric acid on the tin; no similar effect is produced by a solution of stannous chloride containing no free acid. It is also dependent on the energy developed by the diffusion of the acid into the supernatant water, neither cause alone being sufficient to electrolyse the stannous chloride.

Similar phenomena are observed with cadmium chloride and cadmium, the metal being attacked with difficulty by very dilute hydrochloric acid, but zinc, which is easily attacked by the dilute acid, does not give similar results. Nickel gives negative results, probably because the surface of the metal becomes polarised, and antimony and bismuth give negative results because they are not attacked by hydrochloric acid. C. H. B.

**Solidification of Dilute Solutions of Antimony in Tin.** By F. W. KÜSTER (*Zeit. physikal. Chem.*, 12, 508—513).—Heycock and Neville (*Trans.*, 1890, 376) were the first to point out that the solidifying points of dilute solutions of antimony in tin are higher than that of pure tin, a result which they explain by assuming the formation of solid solutions in these cases. The author shows that this is

most probably an instance of isomorphous mixture similar to those which he has himself investigated (Abstr., 1890, 1209). H. C.

**Action of Water on Disodium Platinum Thioplatinate.** New Thioplatinum Salts. By R. SCHNEIDER (*J. pr. Chem.*, [2], 48, 411—424; compare Abstr., 1892, 944).—When disodium platinum thioplatinate,  $2\text{Na}_2\text{S}_2\text{PtS}_2$  (*Annalen*, 138, 618) is heated with water, with exclusion of air, a deep-red solution and an insoluble residue are obtained. The solution contains *sodium thioplatinosate*,  $\text{Na}_2\text{PtS}_2$ , which, however, is speedily decomposed in accordance with the equation  $3\text{Na}_2\text{PtS}_2 + 4\text{H}_2\text{O} = 2\text{H}_2\text{PtS}_2 + \text{Na}_2\text{PtS}_2 + 4\text{NaHO}$ . The insoluble residue consists of the salt *sodium platinum thioplatinate*,  $\text{Na}_2\text{S}_2\text{PtS}_2$ , a microcrystalline, kermes-brown powder, which is decomposed by air with the formation of sodium carbonate and platinum bisulphide, and by hydrochloric acid with liberation of the corresponding acid,  $\text{H}_2\text{S}_2\text{PtS}_2$ . A. G. B.

## Mineralogical Chemistry.

**Native Copper from Yunnan (China).** By W. GOWLAND (*Chem. News*, 68, 307).—A specimen of remarkably tough native copper, consisting of a flat, nodular nucleus, without crystalline structure, and weighing 208.6 grams, but encircled by incrusting layers of cuprite and green copper carbonates weighing 89.5 grams, was obtained from an outcrop in the province of Yunnan, China. The metal was found to be free from gold, lead, arsenic, antimony, bismuth, nickel, and cobalt, but to contain 0.028 per cent. of iron and 0.026 per cent. of silver; it being purer than the electrolytic copper at the author's disposal, a direct determination of copper was not made, but by difference the percentage of copper was found to be 99.946; it therefore surpasses in purity many specimens of native copper hitherto examined, and in fact may be classed with the Lake Superior and Chilian specimens. D. A. L.

**Nickel Arsenide.** By E. WALLER and A. J. MOSES (*Jahrb. f. Min.*, 1894, i, Ref. 17, from *School of Mines Quart.*, 14, 49—51).—The ore from a mine 18 miles from Silver City, New Mexico, consists of dendritic native silver, enclosed in a grey, brittle arsenide, which is found in a matrix of spathic iron ore. The hardness of the nickel compound is 5, its streak black, and its structure granular. Analysis gave results which, on the assumption that silica and silver were present as impurities, were as follows:—

As.	Ni.	Co.	Fe.
78.67	12.25	6.16	2.92

These results correspond with those demanded by the formula for

skutterudite, in which cobalt is replaced by nickel and iron. The authors, therefore, propose the name of *nickel-skutterudite* for this mineral. B. H. B.

**Natural Oxides of Manganese.** By A. GORGEU (*Bull. Soc. Chim.*, [3], 9, 650—661).—*Manganites*.—Four well-crystallised samples of manganite from Ilefeld (Hartz) gave analyses as follows:—

	SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .Al <sub>2</sub> O <sub>3</sub> .	BaO.	PbO,CuO.	CaO.	K <sub>2</sub> O,Na <sub>2</sub> O.
I	0.25	0.35	0.15	0.10	0.10	0.30
II.	0.45	0.25	0.30	0.10	0.20	0.20
III.	0.15	0.30	—	0.10	trace	0.15
IV.	0.05	0.25	—	0.05	0.15	0.25

	MnO.	O in excess.	H <sub>2</sub> O.	Total.
I.	79.40	9.25	10.40	100.30
II.	79.35	9.40	10.10	100.35
III.	79.90	9.15	10.45	100.20
IV.	80.05	10.15	9.40	100.35

II has sp. gr. 4.34, hardness 3.5; III has sp. gr. 4.39, hardness 3.5.

The percentages of water, and of oxygen in excess of that required to form MnO agree with the formula,  $\text{MnO}_2, \text{MnO}, \text{H}_2\text{O}$ , excepting sample IV which appears to have begun to pass into pseudomorphic pyrolusite. The mineral is represented as manganous hydrogen manganite, because concentrated boiling nitric acid dissolves half the manganese on repeated treatment of the very finely powdered mineral.

*Hausmannites*.—Three samples from Ilmenau were examined; they each gave a red streak and appeared to be free from other oxides of manganese. The most noteworthy point is the presence of zinc oxide, not hitherto noticed excepting in the silicates, although the author has found 1—2 per cent. in diallogite from Dietz. The outer friable portion of sample I contained 8.30 per cent. of zinc oxide. Analyses gave:—

	SiO <sub>2</sub> .	P <sub>2</sub> O <sub>5</sub> .	SO <sub>3</sub> .	CO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	K <sub>2</sub> O,Na <sub>2</sub> O.
I.	0.30	trace	trace	trace	0.30	0.10	—	0.40
II.	1.45	0.05	0.10	0.15	0.70	0.55	0.45	0.20
III.	0.13	—	—	—	—	0.20	—	trace

	ZnO.	MnO.	O.	H <sub>2</sub> O.	Total.
I.	8.60	83.40	7.05	0.05	100.20
II.	1.00	88.10	6.65	trace	99.40
III.	7.20	85.40	7.03	0.16	100.12

II has sp. gr. 4.77; III has sp. gr. 4.91, hardness 4.5—5.

Allowing for the oxide of zinc, concentrated nitric acid extracts two-thirds of the manganese; hence the formula of the mineral is  $\text{MnO}_2, 2\text{RO}$ , where R represents Mn partly replaced by Zn.



**Braunites.**—Two well-crystallised specimens of braunite were analysed:—I from Saint-Marcel (Piedmont), hardness 6—6·5; sp. gr. 4·76; and II from Schwarzenburg, hardness 6·0; sp. gr. 4·83. No. I is the only oxide examined in which cobalt occurs.

	Gangue.	SiO <sub>2</sub> .	MnO.	O.	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	PbO,CuO.	CoO.
I.	2·80	9·40	74·68	7·50	3·80	0·50	0·15	0·30
II.	0·60	8·15	80·40	8·35	0·30	1·20	0·85	—

	MgO.	K <sub>2</sub> O,Na <sub>2</sub> O.	BaO.	P <sub>2</sub> O <sub>5</sub> .	H <sub>2</sub> O.	Total.
I.		1·00	trace	0·05	0·20	100·30
II.	trace	0·20	0·20	—	0·20	99·65

These analyses indicate the formula  $(\text{MnSi})\text{O}_2\text{RO}$  for braunite, where  $\text{SiO}_2$  partly replaces  $\text{MnO}_2$  and R is chiefly manganese. Boiling dilute solutions of soda or potash have very little action on finely powdered braunite; hence silica is not present in the free state. As the mineral is completely decomposed by hydrochloric acid, rhodonite ( $\text{SiO}_2, \text{MnO}$ ) is not present. Dilute nitric acid (1:9) has hardly any action on the Saint-Marcel braunites; hence tephroïte ( $\text{SiO}_2, 2\text{MnO}$ ) is absent. Rammelsberg's formula,  $\text{SiO}_2, \text{MnO}_2 + 2(\text{MnO}_2, 2\text{MnO})$ , does not correspond with the above analyses.

The gangue has been deposited later than the main substance in each of the minerals examined, for the crystals show no evidence of penetration by the gangue, whereas the gangue surface corresponds with the projecting angles of the mineral crystals. W. T.

**Heintzite.** By O. LÜDCKE (*Jahrb. f. Min.*, 1894, i, Ref. 19; from *Zeitschr. f. Naturw.*, 1892, 1—8).—The author admits that his heintzite from the pinnoite of Stassfurt (Abstr., 1891, 528), Feit's microcrystalline kaliborite from Schmidtmannshall (Abstr., 1892, 791), and Milch's hintzeite (Abstr., 1891, 528) do not differ from one another. The composition of the three is  $2\text{K}_2\text{B}_2\text{O}_{10} + 9\text{MgB}_4\text{O}_7 + 39\text{H}_2\text{O}$ . Crystallographical measurements support this view. The name of heintzite has priority. B. H. B.

**Microchemical Investigation of Minerals.** By J. LEMBERG *Jahrb. f. Min.*, 1894, Ref. 7; from *Zeit. deutsch. geol. Ges.*, 1892, 224—242).—The author describes various microchemical tests for distinguishing scapolite, hauyn, eudialyte, chabasite, and other minerals. B. H. B.

**Cordierite in an Eruptive Rock of South Africa.** By G. A. F. MOLENGRAFF (*Jahrb. f. Min.*, 1894, i, Mem. 79—91).—The rock described was obtained from the Cornelis River, near Harrismith, in the Orange Free State. It resembles most closely a diabase, and apparently forms a dyke in the Stormberg beds. Under the microscope, it is seen to be composed of glass in which crystals of spinel, cordierite, and augite occur. Analysis of the rock gave the following results.

SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O
64.54	0.79	19.16	7.23	3.39	2.47	0.57	1.13

These results correspond with those given by Osann for the cordierite-bearing mica andesite of Hoyazo. The South African rock increases the far from numerous examples of the occurrence of cordierite in eruptive rocks.

B. H. B.

**Melanite from Missouri.** By E. HAWORTH (*Zeit. Kryst. Min.*, 22, 428; from *Proc. Kansas Acad. Sci.*).—Melanite occurs in brownish-black crystals in cavities produced by solfataric action on a basic vein rock on the eastern fork of the Black River, Reynolds Co. The rock consists of trichlinic feldspar and green fibrous hornblende in a vitreous ground mass. Analysis of the melanite gave

MnO	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	Total
0.20	29.35	5.53	30.71	0.63	100.30

Its sp. gr. is 3.6. This is the first recorded occurrence of garnet in Missouri.

B. H. B.

**Iron Ore Deposit in North Sweden.** By W. PETERSSON and H. SJOGBREN (*Jahrb. f. Min.*, 1894, i, Ref. 88—89; from *Geol. Fören. Förh.*, 15, 45—63, 140—143).—The deposit described, known as the Routivare Iron Mountain, is situated about 9 miles from Quickjokk, in the Swedish province of Norrbotten. The ore (Analysis I) consists of titaniferous magnetite associated with green spinel, olivine, and talc. The rock (Analysis II) in which it occurs is a highly altered gabbro.

	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MnO	MgO	CaO
I.	4.08	14.25	6.40	0.20	33.43	34.58	0.45	3.89	0.65
II.	47.37	0.25	23.22	0.39	—	6.42	0.28	8.67	6.86
			K <sub>2</sub> O	Na <sub>2</sub> O	H <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>			
			I. 0.15	0.29	1.32	0.016			
			II. 0.63	3.25	3.25	—			

The mineralogical constituents of the ore are as follows. (1) Titaniferous magnetite, the main component; (2) ilmenite; (3) spinel; (4) olivine; (5) pyroxene; (6) chlorite; and (7), as accessory constituents, magnetic pyrites and apatite.

B. H. B.

**Diabase from Rio de Janeiro.** By E. O. Hovey (*Jahrb. f. Min.*, 1894, i, Ref. 80—81; from *Min. petr. Mitth.*, 13, 211—221).—In the vicinity of Rio de Janeiro, numerous veins of diabase occur, whose width varies from a few inches up to 20 yards. The structure and character of these veins vary according to the thickness from the gabbro structure, with holocrystalline development in the widest, through the ophitic to porphyritic texture and hypocrySTALLINE development in the narrowest. The author gives the results of analyses of the two extreme varieties. Augite occurs in two forms, namely, ordinary diabase-augite and augite resembling salite. A com-

parison of true salite from Sala, in Sweden, proves, however, that the salite-like augite of the diabase of Rio de Janeiro, New Haven, New Jersey, and Cape Blomedon is not salite. B. H. B.

**Sulphuretted Water from Alexeiewsk.** By N. SATTZEFF (*J. pr. Chem.*, 49, 518—521).—Alexeiewsk is about 20 versts from Samara and 5 to 6 from Schmischlaewka. The mineral water is clear and colourless, and has a strong odour of hydrogen sulphide, a faintly saline taste, and a faintly acid reaction. On exposure to air, it becomes milky, through separation of sulphur, accompanied by a flocculent, black precipitate. The sp. gr. is 1.00141 at 14°. The temperature of the spring is 9.3°. The water contains in 10,000 parts

$K_2SO_4$	$Na_2SO_4$	$Na_2S_2O_3$	$CaSO_4$	$CaCO_3$	$MgSO_4$	$MgCl_2$
0.1556	1.1302	0.1036	13.5843	2.7287	1.7706	0.2550
		$SiO_2$	$Fe_2O_3$	$SH_2$		
		0.1387	0.1083	0.1354		

E. C. R.

**Water and Sea-bottom Deposits from the Eastern Mediterranean.** By K. NAITERER (*Monatsh.*, 14, 624—673; compare *Abstr.*, 1893, ii, 216).—The author gives details of analyses of water and sea-bottom deposits, examined during the voyage of the ship "Pola" in the Eastern Mediterranean during 1893. G. T. M.

## Physiological Chemistry.

**Respiratory Exchange.** By A. MAGNUS LEVY (*Pflüger's Archiv*, 55, 1—126).—This is a very complete account of experiments on animals and men, to show the effect of inanition and diets of different kinds—fats, carbohydrates, proteid, bone, meat, mixed diet—on the respiratory interchanges. The calorimetric value of foods is also discussed. The methods of experiment are fully described. The most important result appears to be the absolute and relative increase of gas exchange and strength, if a proteid diet is continued for some time. W. D. H.

**Absorption and Elimination of Hydrogen and Nitrous Oxide.** By N. GRÉHANT (*Compt. rend. Soc. biol.*, 1893, 616—618).—A dog was allowed to breathe a mixture of hydrogen and oxygen (4 to 1); five minutes after, some blood was collected, and it was found that the nitrogen normally obtainable from blood was replaced by hydrogen; in a few minutes this was replaced by nitrogen when the dog was allowed to breathe air again.

Another animal was allowed to breathe a mixture of 126 litres of nitrous oxide and 33 of oxygen. The blood gases obtained from 100 c.c. of blood amounted to 79.2 c.c., of which 42.8 was carbonic anhydride, 7.8 oxygen, 2.1 nitrogen, and 26.4 nitrous oxide. The

mixture did not produce anæsthesia, on account of the admixture with oxygen, as P. Bert showed. The animal was then allowed to breathe air, and the blood gases analysed at intervals; the quantity of carbonic anhydride and of oxygen fell and rose respectively to the normal, while the foreign gas rapidly disappeared, so that, in half-an-hour's time, none was left in the blood.

W. D. H.

**Pancreatic Ferments.** By A. DASTÈF (*Compt. rend. Soc. Biol.*, 1893, 648—651).—The experiments described show the independence of the two principal ferments contained in pancreatic juice, amylopsin, and trypsin. Three hypotheses are advanced as possible explanations; these are as follow:—

1. The amylolytic ferment is more soluble and diffusible than the proteolytic ferment, and so less firmly held by the glandular cells. The first macerations of the gland substance remove it almost completely.

2. The production of ferments by the pancreatic cell is successive; it is an operation of two acts, of which the first is the formation of amylopsin, the second of trypsin.

3. The two ferments are produced at the same time, but the tryptic one is in the condition of zymogen, only acquiring its fermentative activity after more prolonged contact with the products of the cellular activity of the gland.

W. D. H.

**Conversion of Maltose into Dextrose.** By M. C. TEBB (*J. Physiol.*, 15, 421—432).—Dried pancreas, mucous membrane of the small intestine, Peyer's patches, lymphatic glands, salivary glands, liver, kidney, stomach, spleen, and striated muscle possess the power of converting maltose into dextrose. The relative activities are expressed in the following numbers:—The proportion of maltose to dextrose in similar specimens being for the intestine 1 : 3·21; for the spleen, 1 : 1·35; for lymphatic glands, 1 : 0·93; for the liver, 1 : 0·8; for Peyer's patches, 1 : 0·64; for the kidney, 1 : 0·66; for the stomach, 1 : 0·45; for pancreas, 1 : 0·31; for the salivary glands, 1 : 0·21; for muscle, 1 : 0·2. The small intestine is, therefore, the most active. Serum, bile (slightly), and Benger's pancreatic fluid (slightly) also act in the same way. Peyer's patches, to which Brown and Heron attributed a powerful action in this direction, are seen to be very feeble.

W. D. H.

**Action of Carbonic Anhydride on the Diastatic Ferments of the Animal Body.** By W. EBSTEIN and C. SCHULZE (*Virchow's Archiv*, 134, 475—500).—The ferments investigated were the diastatic ferments of saliva, of the pancreas, blood-serum, muscle, kidney, and liver. In a neutral solution, carbonic anhydride hinders their activity; it appears to act like other weak acids in a corresponding degree of dilution, although in a few experiments with saliva a slight increase in its activity was noted.

In an alkaline solution, carbonic anhydride neutralises some of the alkali, and thus increases the activity of the ferment. In an alkaline solution of 0·021 per cent. sodium carbonate, or 0·015 per cent. disodium hydrogen phosphate, certain salts play the same rôle as

carbonic anhydride, neutralising the hindering action of the alkaline solution. The salts found in human blood-serum act thus, especially sodium chloride, and in a smaller degree, magnesium phosphate,  $\text{MgHPO}_4$ , also.

Acidity equal to 0.01 per cent. lactic acid stops the action of the diastatic ferments of the animal body. W. D. H.

**Influence of Chloroform on Artificial Gastric Digestion.** By DUBS (*Virchow's Archiv*, 134, 519—540).—Chloroform has been recommended by E. Salkowski (*Deutsch. med. Woch.*, 1888, No. 16) as a means by which organised ferments can be killed and the unorganised ferments left still active. Bertels (*Virchow's Archiv*, 130), however, found that under certain circumstances chloroform hinders the activity of pepsin in artificial digestion mixtures. This question is taken up in the present paper with the following results:—Chloroform increases the activity of pepsin in acid solutions in small doses, but hinders it in large doses; this appears to be due to the fact that large doses of chloroform precipitate pepsin. The same is true for hydrochloric acid extracts of the gastric mucous membrane, except that a greater concentration of chloroform (0.6 to 0.7 per cent.) is necessary to produce the harmful effect on the fermentative action. This difference depends on the presence of proteid matter in the extracts of the mucous membrane. The harmful influence of passing a stream of air through the mixture is quite analogous. W. D. H.

**Source of Animal Heat.** By M. RUBNER (*Zeit. Biol.*, 30, 73—142).—This paper contains (1) a very complete dissertation on the various views held by physicists and physiologists as to the source of animal heat from the time of Lavoisier onwards; (2) a description of the methods of animal calorimetry and of the special precautions taken in the present experiments; (3) a full account of experiments on animals on different diets. The following table gives a summary of the results obtained.

Condition.	No. of days.	Total of the calculated heat production.	Total of the heat production by direct estimation.	Mean percentage difference.
Hunger .....	5	1296.3	1305.2	} -1.42
	2	1091.2	1056.6	
Fed on fat .....	5	1510.1	1495.3	} -0.97
Fed on meat and fat .....	8	2492.4	2488.0	
	12	3985.4	3958.4	} -0.42
	6	2249.8	2276.9	
Fed on meat....	7	4780.8	4769.3	} +0.43

In the whole 45 days, the amount found by the calorimeter was only 0.47 per cent. less than that reckoned from the heat value of the food given. The food given is ultimately the only source of animal heat.

The close agreement between the heat production within and without the body is seen from the following numbers.

Heat value of 1 gram of dry substance

	Burnt in the body.	Burnt in Thompson's calorimeter.
Flesh (1) .....	4.059	4.000
" (2) .....	4.007	4.000
Fat (1) .....	9.334	9.423
" (2) .....	9.353	9.423

This is not surprising nor anything new in relation to fat; but with regard to meat, consisting as it does so largely of proteid, the close correspondence of physical and physiological heat values is very noteworthy.

W. D. H.

**Lymph Formation during Muscular Work.** By H. J. HAMBURGER (*Zett. Biol.*, 30, 143—178).—The composition of the lymph which flows from a lymph fistula in the neck of the horse is not quite constant. It is the proportion of water to solid constituents which chiefly varies; during the night, there is an increase of water due to diminished metabolism. One must, therefore, carefully distinguish between day and night lymph. After food, the lymph is increased in quantity three or four times; it is, therefore, necessary to distinguish between the lymph of rest and during or after feeding. Those constituents of the food, such as alkaline salts, which have a water-attracting power, appear to be especially potent in producing an increase in the quantity of lymph. The increase of lymph production cannot always be explained by rise of blood-pressure in the capillaries and veins, for if a horse is made to work, producing a fall of blood-pressure in the carotid, the lymph flows in greater quantity than when the animal is at rest, and the quantitative composition of the lymph of work is different from that of rest, the percentage of solids falling, but the water-attracting constituents (chlorine and alkali) rising.

Even where increased flow of lymph and rise of blood-pressure go together, the first cannot be due to the second, as the composition of the lymph and of the blood-serum show no correspondence. This is against the filtration theory of lymph-formation.

Normal lymph has a much greater osmotic equivalent than the serum of the blood.

In a dead animal, clear lymph continues to flow from the fistula for 15 minutes or more. These facts are also against the filtration theory. It appears probable that the formation of lymph is due to the excitation of the capillary endothelium by the metabolic products of the tissues.

W. D. H.

**Elementary Composition of Ox Flesh.** By P. ARGUTINSKY (*Pflüger's Archiv*, 55, 345—365).—Flesh was dried, the fat and

glycogen being removed. The percentage composition of the residue, mean of five analyses, was as follows:—C, 49·6; N, 15·3; H, 6·9; O and S, 23·0; ash, 5·2; C : N, 3·24.

W. D. H.

**Formation of Sugar in the Liver.** By M. BIAL (*Pflüger's Archiv*, 55, 434—468).—From a review of the literature of the subject, and from the author's own experiments, he draws the conclusion that the teaching of Claude Bernard on the *post-mortem* formation of sugar in the liver is amply confirmed. It is formed at the expense of the glycogen. Sergen considers that the sugar has its source in other substances, such as peptone; but adequate reasons are given to show that this is not the case. Liver substance mixed with peptone solution never yields sugar.

The change of glycogen into sugar is further produced by a diastatic ferment, and this is believed to be the same as that found in the blood and lymph.

The fact that sugar is formed from glycogen does not, of course, exclude its possible formation from proteid.

W. D. H.

**Asparagine in the Nutrition of Herbivora.** By H. WEISKE (*Zeit. Biol.*, 30, 254—278).—Considerable discussion has occurred as to the part, if any, asparagine plays in nutrition, especially as to whether or not it is to be regarded as a proteid-sparing food. The present contribution to the subject is grounded on experiments on rabbits. These show that asparagine exercises a good effect on the animals, that it probably does, under certain circumstances, act as a proteid-sparing food, but that its beneficial effect may be, in part, due to its action on the digestive apparatus; it certainly appears to favour the digestion of starch.

W. D. H.

**Substance resembling Strychnine in the Muscles of Tetanised Animals.** By J. COURMONT and M. DOYON (*Compt. rend. Soc. Biol.*, 1893, 714—715).—Muscle rendered tetanic by subcutaneous injection of the soluble products of the Nicolaier's bacillus (after a constant period of incubation) contains a substance which, like strychnine, produces contraction without incubation. This substance can be extracted from the muscles by means of water, and the aqueous extract produces symptoms resembling those caused by strychnine. This substance is considered to be the cause, not the result, of the muscular contraction.

W. D. H.

**Estimation of Proteids and Extractives in Cow's and Human Milk.** By I. MUNK (*Virchow's Archiv*, 134, 501—519).—The amount of proteid in milk is most rapidly and accurately obtained by estimating, according to Kjeldahl's method, the amount of nitrogen contained in the precipitated proteid. After precipitation of the proteid by alcohol, from one-fifteenth to one-thirtieth of the proteids of cow's milk remain in solution. Tannin and copper hydroxide (at the boiling temperature) precipitate the proteids entirely, and of the two precipitants the copper method is recommended as the more rapid. Fresh cow's milk contains, in 100 parts, 0·022 to 0·034 part of extractive nitro-

gen; human milk, 0.014—0.026 part. The proportion of extractive nitrogen to total nitrogen is 1:16 in cow's milk; 1:11 in human milk.

If the total nitrogen in milk is determined by Kjeldahl's method, sufficient accuracy is usually obtained for the proteid nitrogen by multiplying the total nitrogen by 0.94 and 0.91 in cow's and human milk respectively.

The precipitated proteids consist of casein, albumin, and globulin; the ash free product contains 15.76 per cent of nitrogen. If the nitrogen found by Kjeldahl's method is multiplied by 6.34, the amount of proteid is obtained. Sebelien gives the multiplier as 6.37 (Abstr., 1889, 450).  
W. D. H.

**Human Bile.** By O. HAMMARSTEN (*Kön. Ges. der Wiss. Upsala, Separat-abzug*, 1893).—This paper contains careful analyses of human bile. The principal new point is that the mucin is true mucin, not nucleo-albumin, as in ox-bile.  
W. D. H.

**Work of the Kidney.** By W. H. THOMPSON (*J. Physiol*, 15, 433—448).—A full account of experiments of which a preliminary statement has already been made (Abstr., 1893, ii, 542).  
W. D. H.

**Elementary Composition of Dog's Urine on Flesh Diet.** By F. MEYER (*Pflüger's Archiv*, 55, 212—229).—After allowance is made for the ash, the following table gives the percentage elementary composition of the organic material in the urine at different periods.

	6½ hours after meal.	Fasting condition.	7 hours after meal.	24 hours urine.	Mean.
C .....	23.40	21.60	22.51	22.05	22.5
H .....	6.91	6.73	6.67	6.70	6.8
N .....	39.02	39.57	39.74	39.66	39.4
O .....	30.67	32.10	31.08	31.59	31.3
C.N....	0.60	0.55	0.57	0.56	0.57

W. D. H.

**The Ferrocyanide Test for Urine.** By J. P. KARPLUS (*Chem. Centr.*, 1893, ii, 496; from *Centr. klin. Med.*, 14, 577).—In testing urine for albumin by means of potassium ferrocyanide and acetic acid, a yellow coloration is frequently observed, for which no explanation has hitherto been given. As it was not improbable that the reaction might be due to the presence of nitrites, the author has examined a large number of samples of urine from healthy and diseased persons, and finds that when quite fresh none of these contain nitrites, but that when the urine has remained for periods of upwards of 24 hours, the presence of nitrites may frequently be detected.

Fresh urine from jaundice patients was found to contain no nitrites, but 6 out of 12 samples which had been kept became green on addition of acetic acid, and all these, after removal of the bile pigments, gave the nitrite reaction. In testing for biliprasin in such urine, the



absence of nitrites must, therefore, first be proved. In the urine of patients taking sodium iodide, free iodine occurred together with nitrites.

The urine bacterium recently described by the author has, in addition to its action in forming hydrogen sulphide and probably methylic mercaptan, the property of reducing nitrates to nitrites.

H. G. C.

**Metabolism in Fever.** By R. MAY (*Zeit. Biol.*, 30, 1—72).—The development of heat is increased in the febrile condition; this depends, during hunger, on an increased decomposition of proteid, but it can be lessened by the administration of carbohydrates.

Glycogen disappears in fever more rapidly than at the normal body temperature. The ratio N : C is altered in the urine of fever, febrile urine being richer in carbon.

The increased proteid metabolism in fever is, in the chief place, due to the increased need of the organism for carbohydrates. The degeneration of the cells in causing an increased output of nitrogen is only of secondary importance.

W. D. H.

**Chemical Composition of a Lipoma.** By O. SCHULZ and G. SCHWALBACH (*Pflüger's Archiv*, 55, 231—239).—The fatty tumour investigated contained 22 per cent. of water, 2.25 of connective tissue, 75.75 of fat. The fat contained 7.31 per cent. of free fatty acids and 92.69 of neutral fats. After saponification, 100 grams of the fat yielded 94 grams of fatty acids, and 9.9 grams of glycerol. In the fatty acid mixture the amounts per cent. present were : Oleic acid, 65.57; stearic acid, 29.84; and palmitic acid, 4.59. Cholesterol was present in appreciable quantity.

W. D. H.

**Physiological Action of Pentoses.** By W. EBSTEIN (*Virchow's Archiv*, 134, 361—363; compare *Abstr.*, 1892, 1506, and 1893, ii, 427).—A further contribution to the polemical aspect of this subject, in answer to criticisms raised by Cremer.

W. D. H.

## Chemistry of Vegetable Physiology and Agriculture.

**Tuberculin.** By W. KÜHNE (*Zeit. Biol.*, 30, 221—253; compare *Abstr.*, 1893, i, 233).—Koch's purified tuberculin contains about 10 per cent. of proteid matter, and it is to this and the changes it undergoes under variations of culture, that the present communication chiefly relates. The separation of the proteids from one another by neutral salts was similar to that usually adopted, and the properties and tests for each are fully described. There were found (1) an albuminate; (2) special albuminoses, for which the name *acro-albumoses* is proposed; (3) a deutero-albumose; and (4) traces of peptone. About one-fifth of the solid matter present is mineral in nature. Koch's tuberculoicin appears to contain small quantities of

the same substances; but, if these are removed by alcohol, the substance is not rendered wholly inactive.

W. D. H.

**Presence of a Diastatic Ferment in Green Leaves.** By S. N. VINES (*Ann. Agron.*, 19, 555; from *Annals of Botany*, 5, 409—412) — Wortmann, not finding a diastatic ferment in green leaves, in which, nevertheless, saccharification of starch is very active, attributed saccharifying power to the living protoplasm itself. The author cites the following experiment to prove that leaves do contain a certain quantity of diastase. 500 grams of grass were crushed in a mortar with 500 c.c. of water, and the liquid allowed to remain for four hours, after which six mixtures were made, thus:—(1) 50 c.c. extract and 50 c.c. thin starch paste; (2) the same, but subsequently boiled; (3) the same, but with a little thymol added; (4) the same, but with 5 grams of boric acid added; (5) 50 c.c. of extract and 50 c.c. of distilled water; (6) 50 c.c. of starch paste and 50 c.c. of distilled water.

On the following day, the reducing sugar present in each solution was determined by Fehling's solution, when the following amounts of sugar, in grams per 100 c.c., were obtained: (1) 0.793; (2) 0.450; (3) 0.740; (4) 0.690; (5) 0.444; (6) none.

It appears, by comparing Nos. 2 and 5 with No. 1, that about 0.34 gram of sugar was formed by the action of the diastase in the green grass.

J. M. H. M.

**Soluble Ferments secreted by *Aspergillus niger* and *Penicillium glaucum*.** By E. BOURQUELOT (*Compt. rend. Soc. biol.*, 1893, 653—654).—These moulds, grown in Raulin's liquid, secrete a large number of soluble ferments; thus in *Aspergillus*, a diastase, an invertin, a maltase, a trehalase (found also in several other fungi), an inulase, and an emulsin (in small quantities) were found. In *Penicillium*, there were found the same, some in only small proportions; emulsin, however, is not mentioned as being present. It is added that, in certain conditions of culture, proteolytic ferments are also formed.

W. D. H.

**Non-organised Active Proteid Material.** By T. BOKORNY (*Pfuger's Archiv*, 55, 127—142).—Inactive proteid is the storage proteid used in the nutrition of growing plants. The term active proteid is applied to that in the cell protoplasm, and it is termed non-organised, as it occurs there in granules (proteosomes). A large number of plants were investigated by microscopic and microchemical analysis. The proteid nature of the granules is readily demonstrable by these means. Their behaviour towards ammonia and caffeine distinguishes them from ordinary non-living albumin, which is indifferent to these reagents; they also show the power of reducing silver salts. The substance is considered to play the part of reserve material for the growth of cells and organs.

W. D. H.

**Evolution of Free Nitrogen during the Fermentation of Horse Excrement. Influence of Urine on the Formation and Volatilisation of Ammonia during the Fermentation of Solid**

**Animal Excrement.** By S. JENTYS (*Bied. Centr.*, 22, 801—803; from *Bull. Akad. Sciences de Cracovie*, 1892, 303 and 310).—The results of the author's experiments indicate that a loss of nitrogen may occur during the fermentation of horse excrement. The conditions on which this loss depends are unknown, but there is some reason to suppose it to be due to specific organisms, especially as there are microbes which are known to liberate nitrogen from its compounds. It seems certain that the nitrogen evolution does not depend on the presence of previously formed nitric acid, inasmuch as in this case there would be a greater evolution in absence of oxygen.

The presence of urine does not seem to be favourable to change in the nitrogen compounds of the solid excrement. The loss of ammonia in the mixed excrement is greater the larger the proportion of urine present. Decomposing solid excrement hinders, to some extent, the evolution of ammonia, which becomes fixed, partly by acids and partly by microorganisms. It is possible that the dilution of the urine has some effect on the loss of ammonia. N. H. M.

**Exchange of Carbonic Anhydride and Oxygen between Plants and Air.** By T. SCHLOESING, jun. (*Compt. rend.*, 117, 756—759 and 813—816; compare *Abstr.*, 1893, ii, 180).—The method of experiment which has been already described (*loc. cit.* and *Ann. Inst. Pasteur*, January, 1893) consisted in growing the different plants in quartz sand in enclosed vessels under conditions which enabled measured amounts of gases to be introduced and removed. Excess of oxygen was absorbed by means of heated copper. Check experiments without plants were made for each series of experiments.

	Carbonic anhydride.			Oxygen.			CO <sub>2</sub> disappeared, O <sub>2</sub> liberated = 1.
	Initial.	Final.	Loss.	Initial.	Final.*	Gain.	
1. Flax .....	1468·0	71·0	1397·0	978·9	2529·6	1550·7	0·90
2. Peas .....	1532·8	790·0	802·8	930·1	1778·3	848·2	0·95
3. White mustard..	3015·5	179·4	2836·1	852·1	4115·0	3262·9	0·87
4. " " †	3707·4	583·4	8124·0	855·8	4415·3	3559·5	0·88
5. Algæ.....	477·8	66·3	411·5	228·8	761·2	532·4	0·77

In the first series a gain of 8 c.c. of carbonic anhydride and a loss of 12 c.c. of oxygen were observed; in the second series losses of 10·3 and 9·7 c.c. of carbonic anhydride and oxygen respectively. These errors are taken into account in the table of results given above.

The peas did not grow well for want of sufficient nitrogen, not having been microbe-seeded.

\* Including amounts absorbed by copper.

† Sodium carbonate mixed with soil.

As a check, the carbon supplied in soil, in seeds, and in the carbonic anhydride was estimated, as well as the final amounts in soil, plants, and carbonic anhydride recovered. The results were as follows:—

Experiment.	1.	2.	3.	5.
C at commencement....	834.4	1088.8	1687.9	265.6
C at conclusion .....	787.0	1090.3	1648.1	256.9
Difference .....	-47.4	+1.5	-39.8	-8.7

The losses in Experiments 1 and 3 are probably due to absorption by the glass, which was always very alkaline. Assuming this to be the case, and applying the correction, the relations  $\text{CO}_2 : \text{O}_2$  would become for (1) 0.84 and for (3) 0.85.

In the case of Experiment 5 with algæ (mainly *Protococcus vulgaris*, with *Chlorococcum infusionum*, *Ulothrix subtilis*, and *Scenedesmus quaaricauda*) the following nitrogen results are given:—Nitrogen gas introduced 863.1 c.c., extracted 863.3 c.c.; gain = 0.2 c.c. The indirect method, in which the initial amounts of nitrogen gas, nitrogen in the soil and in the nutritive solution, and the final amount as gas and in soil and algæ together were determined, gave identical results, namely, 1107.7 milligrams of nitrogen.

N. H. M.

**Chemical Nature of Cytoplasm and Cell Nucleus.** By E. ZACHARIAS (*Chem. Centr.*, 1893, ii, 461; from *Ber. deutsch. Bot. Zeit.*, 11, 293).—The author regards the following points as proved with regard to the distribution of proteid compounds in the cells: the cell protoplasm and cell nucleus consist to a large extent of substances which are insoluble in artificial gastric juice, the greater proportion of these being the chromatin substances of the cell-nucleus (nuclein). In their reactions, the latter agree with the undigested portion of the salmon spermatozoa from which Miescher prepared nucleic acid. The other insoluble portions show different reactions, and are classed together by the author under the name *plastin*.

The cell protoplasm and cell nucleus contain in addition proteids soluble in the digestive fluid, the nucleoli being in many carefully-examined cases especially rich in these substances, whereas cell protoplasm, especially in fully-grown plant cells, frequently contains them in but small quantity.

H. G. C.

**Carbohydrates of the Fruit of the Kentucky Coffee Nut Tree** (*Gymnocladus canadensis*). By W. E. STONE and W. H. TEST (*Amer. Chem. J.*, 15, 660—663).—The fruit consists of a leathery pod from 3 to 10 in. in length, and contains from two to six brown, oval, and very hard seeds embedded in a greenish, waxy pulp or gum. This gum has a sweet but very disagreeable taste, and at the time of ripening is soft and easily removed, although later it becomes horny. It contains no galactose, galactan, or starch, but abundance of soluble reducing sugars and pentosans.

The alcoholic extract yielded cane sugar (15 per cent.),  $[\alpha]_D = 65.4^\circ$ , and glucose (15 per cent.).

The gummy residue, on hydrolysis with dilute sulphuric acid,

yielded an insoluble substance resembling cellulose, and a thick, reducing syrup which gave the furfuraldehyde reaction for pentoses. The osazone melted at 175—180°, indicating a mixture. This was separated by means of alcohol and water into two fractions: the first proved to be glucosazone (m. p. 204—205°), soluble in alcohol but insoluble in boiling water; the second (m. p. 153°) was probably arabinosazone (m. p. 158—160°), insoluble in alcohol but soluble in boiling water. The latter gave abundance of furfuraldehyde when boiled with strong hydrochloric acid, and its alcoholic solution was optically inactive, so that it was not xylosazone. The glucose and arabinose probably exist in the original gum in combination as *gluco-araban*. JN. W

**Sugar from Apple Pectin.** By R. W. BAUER (*Landw. Versuchs-Stat.*, 43, 191).—Apple pectin, extracted with alcohol, was boiled for four hours with 0.5 per cent. sulphuric acid, filtered, and polarised, when a rotation of +17° was observed. The filtrate, treated with an equal volume of alcohol, became clear after being kept for a year, and had an agreeable odour of ethylic malate. After neutralising with baryta, and evaporating the filtered solution under diminished pressure over sulphuric acid until of constant weight, a substance (2.763 grams) was obtained which proved by its optical properties ( $[\alpha]_D = +18.77^\circ$ ) and its osazone (microscopic, gold-coloured needles melting at 170°) to be xylose, produced, by hydrolysis from xylan present in apple pectin. N. H. M.

**Formation of Pectin by the Action of Lime on the Sugar-Cane.** By H. C. P. GEERLIGS (*Chem. Centr.*, 1893, ii, 531; from *Arch. Java Suikerindustrie*, 1893).—The pectin which is always found in the juice of the sugar-cane during the manufacture of sugar is formed by the action of lime on the fragments of the cane which are present. Its formation may be prevented by carefully filtering off the latter, or it may be precipitated with barium chloride in alkaline solution.

The crude wax of the sugar-cane may be purified by recrystallisation from alcohol, and then forms white, crystalline plates melting at 82°, and boiling at 146° [?]. Unlike other waxes, it does not consist of ethereal salts of fatty acids, but is chiefly composed of a saturated alcohol having the formula  $C_{24}H_{48}O$  [?]; the latter, on distillation with soda lime, yields a hydrocarbon melting at 92°, and boiling at 225°. Dumas and Leroy have recently obtained similar results in the case of American sugar-cane wax.

When the syrup from the centrifugals is heated by live steam, a thick froth is formed which may readily be removed, and which otherwise adheres to the sugar, crystallising out on direct evaporation. It has approximately the same composition as the syrup, but contains rather more ash and fat. The froth can only be obtained from a purified syrup to which these impurities have been added, by mixing with them a little bicarbonate, from which it would appear that the evolution of gas is necessary for its formation. In the crude syrup this is probably brought about by the carbonic anhydride evolved in the decomposition of the glucin present.

H. G. C.

**Occurrence and Detection of Indican in Plants.** By H. MOLISCH (*Chem. Centr.*, 1893, ii, 667—668; from *Zeit. Österr. Apoth. Verein*, 31, 524).—Indican only occurs in about 10 phanerogamous species of the vegetable kingdom. Whether a plant contains indican can be rapidly decided by the following test:—Fragments of the plant are boiled for about half a minute in a test tube with 2 per cent. ammonia solution, filtered over a platinum cone, and extracted with a little chloroform. A similar experiment is carried out with 2 per cent. hydrochloric acid. In the presence of indican, one or both of the chloroform extracts is coloured blue. Indican may occur in many of the organs and tissues of the indigo plants, but is mainly found in the foliage leaves. The statements found in the literature of the subject that indican occurs in *Mercurialis perennis*, *Melampyrum arvense*, *Polygonum Fagopyrum*, *Phytolacca decandra*, *Monotropa Hypopitys*, *Fraxinus excelsior*, *Coronilla Emerus*, and *Amorpha fruticosa*, are inaccurate. A chromogen does occur in the organs of the fresh toothwort (*Lathræa Squamaria*), which yields a blue colouring matter with dilute hydrochloric acid; but this is quite distinct from indigo. A. H.

**Amount of Maltose and the Fermentability of Wort and other Extracts.** By O. REINKE (*Bied. Centr.*, 22, 839—840).—Malt dried at 80° contained water (5 per cent.), and extract (73·15 per cent.) yielding 70 per cent. of maltose and 17 per cent. of dextrin after inversion and deduction of the maltose. When very lightly dried, the maltose was 5 per cent. higher and the dextrin 5 per cent. lower. In highly-dried malt, the amounts of maltose and dextrin were respectively 7 per cent. lower and 7 per cent. higher. 90 per cent. of the maltose fermented at 30°.

As regards extracts for the manufacture of spirit, the following percentage results are given for sweet potato extracts:—

	1.	2.	3.	4.
Maltose in extract....	64·84	67·16	60·60	68·09
Dextrin in extract....	14·04	13·46	14·41	15·90
Fermentable maltose..	58·36	60·44	54·54	61·28
In the filtrate:				
Saccharimeter° Ball ..	25·00	20·80	25·10	17·3
Maltose.....	16·21	13·97	14·00	11·78
Fermentable maltose..	14·59	12·57	12·6	10·6
Dextrin.....	3·51	2·80	4·02	2·75

When the fermentation is complete, there is generally only 6 per cent. of dextrin left. When the 90 per cent. of fermentable maltose is calculated as dextrose, and the amount of dextrose corresponding with half the dextrin added, and the whole multiplied by 64·64, the result gives the amount of alcohol to be obtained from the extract.

N. H. M.

**Composition of Seeds and Etiolated Sprouts of Hemp (*Cannabis sativa*) and of Sunflower (*Helianthus annuus*).** By S. FRANKFURT (*Landw. Versuchs-Stat.*, 43, 143—182).—A qualitative examination, the details of which are given, showed the presence

of the following compounds in hemp seeds:—Proteids, nucleïn, and ether indigestible nitrogenous compounds, organic bases, lecithin, cholesterol, glycerides, cane sugar, non-crystalline soluble carbohydrates, hemicellulose, citric acid, cellulose, pentosan, and mineral matters. Detmer failed to find soluble carbohydrates in the seeds (*Physiol. Chem. Untersuchung über d. Keimung ölhaltigen Samen*, p. 38). The quantitative results are next given (per cent.).

Proteids.	Nucleïn. &c.	Lecithin.	Cholesterol.	Glycerides and free fatty acids.
18·63	3·36	0·88	3·07	30·92
Cane-sugar and other soluble carbohydrates.	Crude fibre.	Soluble organic acids.	Ash.	Not determined.
2·59	26·33	0·68	5·551	11·03

As regards the changes which take place during germination, Detmer (*loc. cit.*) showed that the fat diminishes in amount, and is replaced by starch, cellulose, &c. Owing to the difficulty of obtaining large enough quantities of sprouts, the author only made a quantitative examination for certain constituents. Asparagin and two compounds, probably glutamic and glyoxylic acid respectively, were found.

The sunflower seeds and sprouts were more thoroughly investigated. The seeds were separated from the shells, and the two portions, which had the relation 53·6 : 46·4, separately examined. The percentage composition was found to be as follows:—

	Seeds without shell.	Shells.	Whole seeds.
Proteids .....	24·06	1·33	13·50
Nucleïn, &c.....	0·96	—	0·51
Lecithin .....	0·44	—	0·23
Crude fat .....	55·47	1·00	30·19
Cane sugar and other soluble carbohydrates	3·78	—	2·13
Crude fibre.....	2·24	64·54	31·14
Soluble organic acids .....	0·56	—	0·30
Ash .....	3·66	1·93	2·86
Not determined .....	8·83	31·20	19·14

The seeds freed from shells contain also pentosan (soluble, 0·87; insoluble, 1·87 per cent.). They contain no, or almost no, hemicellulose. The shells are very poor in nitrogen. They contain hemicellulose. When the shells are kept in contact with 0·5 per cent. soda for a day, and the residue washed and boiled with 2 per cent. sulphuric acid, a sugar was obtained which, when isolated, proved to be xylose.

The quantitative examination of the etiolated sunflower sprouts showed the presence of asparagine and glutamine, malic acid, and considerable amounts of soluble carbohydrates. Nitrogenous organic bases were present only in very small amounts. Cane sugar, cellulose, hemicellulose, and pentosans were also found. The

percentage composition of the dried sprouts freed from shells was as follows:—

Proteids.	Nuclein, &c.	Asparagine and glutamine.	Lecithin.	Fat.	Cane sugar, &c.
15.00	4.56	4.05	0.85	24.54	14.75
Soluble organic acids.					
	2.43	Crude fibre.	Ash.	Not determined.	
		11.52	4.09	18.21	

In order to compare the composition of the seeds with that of the sprouts, the quantities were calculated on the assumption that the amount of ash in both is practically the same. The results show first a great diminution in the amount of proteids, whilst the insoluble nitrogen compounds (nuclein) increased considerably (0.96 to 4.05). Unlike the etiolated sprouts of vetches and lupins, which contain considerable quantities of nitrogenous organic bases, the sunflower sprouts contained a very small amount. Another difference is the increase of lecithin (0.44 to 0.71 per cent.). Schulze observed a loss in lupins and vetches. The percentage of fat became much lower during germination, whilst the soluble carbohydrates increased. There was no loss of nitrogen during germination. N. H. M.

**Development and Maturation of Cider Apples.** By L. LINDET (*Compt. rend.*, 117, 696—698).—Apples were taken every two weeks (from 24th July to 3rd November) from the same tree and analysed. The average weight of the apples at each date was as follows:—(1) 24th July, 21.5; (2) 7th August, 34.0; (3) 23rd August, 46.0; (4) 7th September, 50.2; (5) 21st September, 60.3; (6) 4th October, 68.7; (7) 18th October, 75.3; and (8) 3rd November, 76.5 grams. The percentage composition of the apples at the different dates was:—

Starch.	Saccharose.	Invert sugar.	Acidity.	Cellulose substance.	Nitrogenous matter.	Ash.
1. 4.8	1.1	6.4	0.5	4.4	—	0.4
2. 4.8	1.2	6.8	0.5	3.1	0.6	0.4
3. 4.9	1.2	8.3	0.4	3.2	0.5	0.4
4. 5.8	2.3	8.3	0.4	2.8	0.3	0.3
5. 3.8	2.5	8.3	0.3	2.8	0.3	0.3
6. 3.3	3.2	8.2	0.2	2.7	0.3	0.2
7. 2.1	3.7	8.6	0.2	2.6	0.4	0.3
8. 0.8	2.9	9.4	0.2	—	0.3	0.2

The apples were green until September 7, at which date the pips began to become coloured. The chief change is in the starch, which, as ripening proceeds, becomes converted into what seems to be a mixture of saccharose, glucose, and levulose. It is possible that a portion of the saccharose had migrated from the leaves, but it is probable that some of it is furnished by the starch. The same disappearance of the accumulated starch, and, coincidentally, an increase of saccharose and invert sugar was also observed in apples allowed to ripen after being taken from the tree. N. H. M.



**Nitrification of Prairie Soils.** By J. DUMONT and J. CROCHETTELLÉ (*Compt. rend.*, 117, 670—673).—Boussingault, and more recently Bréal, have shown that prairie soils contain comparatively small amounts of nitrates, so that the enormous amount of organic nitrogen becomes very slowly available for vegetation. It seemed likely that the slow nitrification is due to insufficient alkalinity. The authors accordingly instituted experiments in which two different soils (containing respectively 6·84 and 5·76 per cent. of humus) were exposed for three or four weeks, after being treated with various amounts (0·1 to 1·0 per cent.) of potassium carbonate, chloride, and sulphate, and sodium carbonate (each alone); check experiments were made in which nothing was added. At the conclusion of the experiments the soils were extracted, and the nitric acid estimated. Similar experiments were made in which arable soils (containing 2·9 and 1·08 per cent. of humus) were treated with the various salts, and exposed for 15 days.

The results of the experiments show that with the rich soils an addition of 0·2 to 0·3 per cent. of potassium carbonate increases nitrification, whilst larger quantities are injurious. Potassium sulphate (0·7 to 0·8 per cent.) gave rise to increased nitrification. Potassium chloride had only a slight effect, the nitric nitrogen per cent. being raised from 0·008 per cent. to 0·01 per cent. with 0·025 to 0·3 per cent. of the salt. Sodium carbonate had no beneficial effect, nitrification being lessened when more than 0·15 per cent. was applied to the soil.

In the case of the experiments with arable soils, in which only one amount of each salt was applied (0·2 per cent.), the best result was obtained with potassium sulphate. It remains to be ascertained what amount of the salt gives the best results. N. H. M.

**Comparative Experiments with various Phosphates.** By O. KELLNER, Y. KOZAI, Y. MORI, and M. NAGAOKA (*Landw. Versuchs-Stat.*, 43, 1—14).—Experiments have already been made on the effect of different phosphates on irrigated soil (*ibid.*, 41, 305). The results now given were obtained on ordinary arable land, consisting, like the irrigated soil, of sand mixed with volcanic ashes, rich in easily decomposable aluminium silicates, iron, and humus, but containing very little lime. The manures employed were double superphosphate (with 47·84 total and 43·65 per cent. of phosphoric acid, soluble in water), precipitated calcium phosphate (with 29·35 total phosphoric acid), basic slag (with 21·75 per cent. of phosphoric acid), steamed bone meal (with phosphoric acid, 23·06; nitrogen, 3·87; and fat, 1·33 per cent.), crude bone meal, freed from fat (phosphoric acid, 19·70; nitrogen, 4·74; and fat, 1·93 per cent.), crude crushed bone (phosphoric acid, 21·66; nitrogen, 4·61; and fat, 14·07 per cent.) and bone ash (containing 30·465 per cent. of phosphoric acid). The experiments were conducted in Wagner's zinc cylinders, 60 cm. in diameter, and 1 m. deep. Calcium carbonate (1000 kilos. per hectare), potassium sulphate (200 kilos. per hectare) and ammonium sulphate (containing 50 kilos. of nitrogen per hectare) were mixed with the soil as well as the phosphates, which were each applied in two

quantities, 50 and 100 to 100 and 200 kilos. per hectare. There were 48 cylinders, six without phosphate and six with each manure (three with the smaller and three with the larger amount). Barley was first sown. After the plants were cut and the stubble mixed with the soil, millet was sown, next wheat, and lastly buckwheat. The total dry substance, and the amount of phosphoric acid removed from the various cylinders is given in tables. The larger amounts of manures gave in every case higher yields than the smaller, but as they did not in every case have their full effect, the results obtained with the smaller quantities are the more suitable for comparison. Taking first into consideration the effect on the first growth (barley), superphosphate gave the highest yield of dry produce, which contained 21.5 per cent. of the total phosphoric acid applied. The next most efficacious manure was steamed bone meal, of which 16.6 per cent. of the total phosphoric acid applied was found in the produce. Then precipitated calcium phosphate, crude bone meal free from fat, crude crushed bone, basic slag, and, lastly, bone ash. The produce obtained under the influence of these manures contained respectively 13.8, 12.4, 12.6, 13.1, and 5.0 of the total phosphoric acid applied. It is noteworthy that the high percentage of fat in the crushed bone (14.07) did not hinder the utilisation of the phosphates.

As regards the effect of the manures on the subsequent growth (millet, wheat, and buckwheat), there was a decided but different effect in each case. The results, which are shown in a curve, indicate a great similarity in the after-effect of the superphosphate, the steamed bone meal, and the precipitated phosphate and also the basic slag, all of which were chiefly utilised by the first two growths. The slight effect produced by the superphosphate and the precipitated phosphate in the after-growths was due to their diminished solubility in contact with the soil, but better results were expected with basic slag. Both the crude bone meal and the crushed bone, which had but little influence on the first crop, had very considerable effect on the succeeding crops, and their action would probably have continued long.

Of the different bone manures applied, the crude crushed bones gave the greatest total yield; next the bone meal freed from fat; and lastly, the steamed bone meal. The results show that, under the prevailing climatological conditions, fat also acts in unlocking the calcium phosphate, although more slowly than the nitrogenous matter.

Bone ash becomes gradually and uniformly available for the roots. It is not suitable for damp rich soils.

N. H. M.

## Analytical Chemistry.

**An Automatic Extractor.** By W. D. HORNE (*Chem. News*, 68, 250).—The following arrangement is devised to effect the delivery of a definite quantity of water in portions of equal volume at regular intervals. A bottle of the desired capacity is fitted with a stopper,

bored with two holes, each carrying an open tube; the tubes pass just through the stopper internally, but externally one of them is short and straight, and terminates with a constricted orifice, whilst the other is bent twice at right angles, and extends down the whole height of the bottle outside. In use, the bottle is filled with water, stoppered, and inverted, and water can then be caused to escape from the short tube at any desired rate by regulating the supply of air admitted through the other tube. This regulated water supply drops into a receptacle suspended below the bottle, and provided with an adjustable inverted siphon inside, by which any required volume of water can be automatically drawn off at a time, and utilised for washing a precipitate or other purpose. D. A. L.

**Lunge's Gas Tables.** By A. LWOFF (*Zeit. angr. Chem.*, 1893, 443—445).—In Lunge's original tables, a correction for pressure down to 710 mm. is given. The author has now also corrected the volumes for pressures varying from 680 to 710 mm. L. DE K.

**Indicators for Titrations with Standard Sulphide Solutions.** By P. WILLIAMS (*Chem. News*, 68, 236).—The author has compared the delicacy of the following reagents when used as indicators for titrations with standard sulphide solutions:—I. A solution of sodium tartrate, treated with a small quantity of caustic soda and lead acetate, and heated until clear. II. A solution of potassium nitroprusside, saturated with soda, evaporated nearly to crystallising, and treated with 4 parts of alcohol, and filtered. With the first reagent 0.0000245 gram, with the second 0.0000982 gram of sodium sulphide in 1 c.c. may be detected. D. A. L.

**Estimation of Dissolved Oxygen in Water.** By C. M. VAN DEVENTER and B. H. JÜRGENS (*Chem. Centr.*, 1893, ii, 546; from *Maandbl. natuurw.*, 18, 72).—The method described depends on the fact that when iodine is set free from potassium iodide by means of free nitrous acid, nitric oxide is formed, but that if dissolved oxygen is present, the latter combines with the nitric oxide, forming  $\text{NO}_2$  or  $\text{N}_2\text{O}_3$ , which in presence of acid liberates a fresh quantity of iodine.

*Note by Abstractor.*—The method is almost exactly identical with that described by Thresh (*Trans.*, 1890, 185), with the modification that instead of carrying out the titration in a current of coal gas, the liquid to be tested is covered with a layer of petroleum.

H. G. C.

**Estimation of Nitrogen in Coal Gas.** By L. LANG (*Chem. Centr.*, 1893, ii, 773; from *J. j. Gasbel.*, 493—494).—20 c.c. of the sample of gas is measured in the Bunte's burette, mixed with 125 c.c. of air, and exploded in a Hempel's pipette. Carbonic anhydride and oxygen are now absorbed as usual, and the remaining nitrogen is measured. Any excess over the amount of nitrogen present in the air is supposed to have been present in the gas. L. DE K

**Adulteration of Basic Slag.** By E. WRAMPPELMAYER (*Landw. Versuchs-Stat.*, 43, 183—190).—Natural phosphorite is sometimes coloured so as to resemble basic slag; finely powdered coal is sometimes added for this purpose. The following methods for detecting adulteration are given:—(1) Estimation of loss on ignition in a Bessler furnace. The loss in old samples of basic slag is slight, whilst with fresh samples there is a gain owing to oxidation. (2) Estimation of substance soluble in warm water after ignition. (3) Determination of sp. gr. Basic slag has a sp. gr. = 1.9 or higher, whilst all the other phosphates examined varied from 1.1 to 1.6. (5) Estimation of phosphoric acid soluble in citric acid (Loges' method) and in ammonium citrate (Petermann's method). Results of examination of various phosphates show that the microscopic examination and sp. gr. alone are generally sufficient for ascertaining whether the slag is genuine or not. In two cases, however, the microscopic examination, solubility in water, citric acid, and ammonium citrate indicated genuine slag, whilst the low sp. gr. and the high loss on ignition clearly pointed to adulteration.

The suspected sample should always first be examined with a microscope, then, if necessary, the loss on ignition and sp. gr. and solubility in water determined, lastly, if any doubt remains, the solubility determined by Loges' and Petermann's methods.

N. H. M.

**Estimation of Carbon in Steel.** By R. LORENZ (*Zeit. angew. Chem.*, 1893, 635—637).—The author, in reply to de Koninck, states that fusion with lead chromate in a current of oxygen at a white heat (*Abstr.*, 1893, ii, 491) causes the complete oxidation of the carbon, and doubts whether the same satisfactory result could be obtained by the use of borax or microcosmic salt, even when mixed with copper oxide.

L. DE K.

**Volumetric Estimation of Silver.** By G. DENIGÈS (*Compt. rend.*, 117, 1078—1081).—The reaction between silver nitrate and potassium cyanide, with formation of silver potassium cyanide, proceeds regularly in presence of ammonia, and the end reaction is made very sensitive by adding a small quantity of potassium iodide to the liquid. The result is not affected by considerable variations in the proportion of ammonia, or by the presence of alkali hydroxides, carbonates, chlorides, bromides, phosphates, &c. It is, therefore, not only a very accurate process for the estimation of hydrocyanic acid or cyanides, but, by using a standard solution of potassium cyanide, it can be employed for the estimation of any silver compound whatever.

A solution of about 10 grams of potassium cyanide per litre is used, and will remain unchanged for many days, its stability, especially in hot solutions, being increased by the presence of excess of alkali.

The quantity of substance taken for analysis should contain about one-thousandth of a gram equivalent of silver, and is dissolved in 10 c.c. of ammonia solution and 5 c.c. of water, with the aid of heat if necessary. The ferrocyanide, bromide, and iodide will not dissolve until the standard cyanide solution is added. The phosphate, arsen-

ate, chromate, oxide, and sulphide should be dissolved in nitric acid and then mixed with excess of ammonia. In all cases the liquid containing a slight excess of ammonia is mixed with 20 c.c. of standard cyanide solution, about 100 c.c. of water, and a small quantity of potassium iodide solution, and decinormal silver nitrate solution is added gradually with constant agitation until a slight, permanent turbidity is produced. The difference between the volume of silver solution required and that required for the 20 c.c. of standard cyanide solution alone, gives the quantity of silver present in the substance.

This process is available for the volumetric estimation of precipitates of silver chloride; the direct estimation of chlorides in liquids of animal origin; the determination of the xantho-uric compounds in urine by precipitation with ammoniacal silver nitrate solution, and estimation of the excess of silver in the filtered liquid; estimation of potassium iodide by precipitation with ammoniacal silver nitrate solution; and estimation of all substances such as acetylenes, arsenic hydride, antimony hydride, aldehydes, carbonic oxide, &c., which are capable of altering the strength of alcoholic, ammoniacal, or acid solutions of silver salts.

C. H. B.

**Electrolytic Analyses.** By F. RÜDORFF (*Zeit. angew. Chem.*, 450—453).—The author, in reply to Classen, objects to the processes given in that chemist's work, and thinks his own methods are more accurate (compare Abstr., 1893, ii, 93—95).

L. DE K.

**Volumetric Estimation of Copper with Sodium Sulphide.** By A. BORNTRÄGER (*Zeit. angew. Chem.*, 1893, 517—524).—The author prepares the sodium sulphide solution by dissolving 40 grams of the commercial sulphide in 1 litre of water. This solution is standardised by means of a solution containing 69.278 grams of crystallised copper sulphate per litre. 10 c.c. of the solution is mixed with a little ammonia, and titrated in the cold with the alkaline sulphide until a drop of the supernatant liquid gives no coloration with acetic acid and potassium ferrocyanide. The process may be used in presence of zinc. The copper solution is rendered alkaline with ammonia, and any iron oxide is filtered off. The addition of the sulphide may at first also precipitate a little of the zinc, but this rapidly redissolves as long as a trace of copper is present. The process may be recommended for the assay of brass, commercial copper sulphate, and a variety of copper sulphate disinfectants.

L. DE K.

**Separation of Lead from Copper by Electrolysis.** By H. NISSENSEN (*Zeit. angew. Chem.*, 1893, 646).—The author states that Rüdorff is wrong in supposing that the electrolytic separation of copper from lead is only successful when the lead is present in minute quantity, and proceeds as follows:—1 gram of copper ore is dissolved in 30 c.c. of nitric acid of 1.4 sp. gr., diluted to 180 c.c. and electrolysed carefully according to Classen's directions. An accurate estimation of the copper is obtained, even in the case of ores containing 12 per cent. of lead to 20 per cent. of copper.

L. DE K.

**Electrolytic Separation of Metals of the Second Group.** By S. C. SCHMUCKER (*Zeit. anorg. Chem.*, 5, 199—210).—The author adds to the solution an excess of bromine to ensure the highest degree of oxidation; tartaric acid is next added, and then an excess of ammonia. The solution, after being put into a platinum dish, is now electrolysed as usual, the strength and duration of the current varying somewhat according to the nature of the metallic salts. For instance, in the separation of copper from tin, the solution containing about 0.1 gram of each metal in 175 c.c. of liquid was exposed to the galvanic action for 17 hours, the current yielding 0.4 c.c. of electrolytic gas per minute. The copper was completely recovered, and perfectly pure.

The tartaric acid method has proved successful in the separation of copper from arsenic, antimony, and tin; cadmium from antimony; cadmium from tin; cadmium from arsenic; cadmium from arsenic, antimony, and tin; bismuth from arsenic; bismuth from antimony; bismuth from tin; bismuth from arsenic, antimony, and tin; mercury from tin; mercury from arsenic; mercury from antimony; mercury from arsenic, antimony, and tin. The author has not, as yet, tried any experiments with lead when mixed with tin, arsenic, or antimony.

L. DE K.

**Estimation of Manganese Oxides by means of Hydrogen Peroxide.** By H. C. JONES (*Compt. rend.*, 117, 781—783).—The method described by Carnot (*Abstr.*, 1893, ii, 427) is only a special case of the general method described by the author (*Amer. Chem. J.*, 12, 275), which is applicable also to the higher oxides of lead.

C. H. B.

**Detection of Nitronaphthalene in Mineral Oils.** By N. LEONARD (*Chem. News*, 68, 297).— $\alpha$ -Nitronaphthalene is added to mineral oils to remove the fluorescence, and may be detected by gently warming and agitating the oil with zinc dust and hydrochloric acid; the characteristic odour of  $\alpha$ -naphthylamine will indicate the previous existence of the nitro-derivative; this may be confirmed by the blue precipitate, quickly changing to purple, obtained when ferric chloride is added to a portion of the acid aqueous solution of the amine previously neutralised with ammonia; also by the production of a yellow colour, changing to crimson with hydrochloric acid, when another portion of this liquid is rendered alkaline with soda, extracted with ether, the ether evaporated from the extract, and the residue dissolved in a small quantity of alcohol and treated with a drop of a solution of sodium nitrite and acidified with acetic acid.

D. A. L.

**Estimation of Cresol or Xylenol.** By F. KEPPLER (*Chem. Centr.*, 1893, ii, 892—893; from *Arch. Hygiene*, 18, 51—66).—A mixture of potassium bromide and bromate is added to the solution containing the cresol. After adding a sufficiency of sulphuric acid, the liquid is filtered through glass wool, and an aliquot part of the filtrate is titrated, as usual, by means of potassium iodide and sodium thiosulphate with starch as indicator.

L. DE K.

**Checking Fehling's Solution.** By A. BOENTRÄGER (*Zeit. angew. Chem.*, 1893, 600—601).—The author has come to the conclusion that the standard solution of invert sugar used to check the Fehling solution should be prepared at the ordinary temperature. Pure saccharose is easily prepared by precipitating a filtered, concentrated solution of sugar candy with alcohol and drying the precipitate. 19 grams of this product is dissolved in dilute hydrochloric acid containing 4.5 per cent. of HCl in a 100 c.c. flask. After standing over night, 25 c.c. is pipetted off, coloured with a little limus, exactly neutralised with alkali, and made up to 1 litre. This solution contains 0.5 per cent of invert sugar. L. DE K.

**Sugar in the Blood.** By F. SCHENCK (*Pflüger's Archiv*, 55, 203—211).—The following method of estimating sugar in the blood is recommended: 50 c.c. of blood is mixed with 50 c.c. of water; to this, 100 c.c. of 2 per cent. hydrochloric acid and then 100 c.c. of 5 per cent. mercuric chloride are added. The mixture is filtered, and the filtrate decomposed with hydrogen sulphide. This is again filtered. 150 c.c. of the filtrate taken, and air passed through it to get rid of the hydrogen sulphide: it is concentrated to 100 c.c., and then titration is performed by Knapp's method. The mercuric chloride appears to give as good results as the more expensive iodide.

When the blood coagulates, the disappearance of sugar is very great; it may be 25 per cent. If kept uncoagulated by an oxalate, the loss is insignificant. If blood is acidified, the loss is practically nil. W. D. H.

**Use of Methylene-blue for the Detection and Estimation of Sugar in Urine.** By N. WENDER (*Chem. Centr.*, 1893, ii, 670—671; from *Pharm. Post.*, 26, 393—397).—Ihl observed that methylene-blue is decolorised, by reduction to the leuco-compound, by invert sugar, dextrose, dextrin, &c., whilst it is not acted on by cane sugar. Urea, uric acid, and the inorganic salts in urine are without action on methylene-blue; creatinine decolorises it with tolerable rapidity; creatine, after boiling for some time, and albumin, when it is present to the extent of some tenths of a per cent. Animal gum and glycuronic acid may also decolorise methylene-blue; concentrated alkalis decolorise it rapidly with separation of the free base, but dilute alkalis do not produce any effect. All normal urines in the undiluted state decolorise alkaline methylene-blue solutions on heating; 1 c.c. normal undiluted urine decolorises 1 c.c. of methylene-blue solution (1:1000). To decolorise the same amount of methylene-blue, about 4.5 c.c. of 10 times diluted normal urine is required, whilst only 1 c.c. of a similarly diluted diabetic urine, containing 0.5 per cent. of sugar, produces the same effect. In order to detect the presence of sugar in urine, the following method is adopted: 5 or 10 c.c. of the urine is diluted to 10 times its volume; 1 c.c. of this solution is then treated with 1 c.c. of aqueous methylene-blue solution (1:1000) and 1 c.c. of normal potash, diluted with about 2 c.c. of water, and boiled over a naked flame for a minute. In the presence of 0.5 per cent. of sugar, total decolorisation takes place. If the coloration remains, the urine may be considered as not diabetic,

Quantitative experiments showed that 1 mol. of methylene-blue is reduced by 1 mol. of dextrose. 1 c.c. of methylene-blue solution, 1:1000 = 0.001 gram methylene-blue would be reduced by 0.005 gram of dextrose. The decolorising power of a normal urine, therefore, corresponds with that of a 0.11 per cent. solution of dextrose. If  $p$  is the percentage of sugar in the urine which has to be determined,  $v$  the dilution factor,  $c$  the number of c.c. of the methylene-blue solution required, then  $p = 0.05 v/c$ .

The determination of sugar in urine is carried out in the following manner. If sugar is found by the qualitative test, the urine is diluted according to its specific gravity.

Sp. gr. ....	1.017—1.025	1.025—1.030	1.030—1.038
	(50 times)	(100 times)	(200 times)

The volume of the diluted urine which is required to exactly decolorise 0.001 gram of methylene-blue is then determined, several titrations being made. 1 c.c. of methylene-blue solution and 1 c.c. of normal potash are put into a test tube, and the urine run in gradually from a burette, the liquid being boiled once or twice. This process is repeated until the exact amount of urine required has been found. The results obtained by the author fall between those given by the polarisation method and by the reduction of Fehling's solution. Owing to the great dilution of the urine, the disturbing influence of the other constituents of urine which are capable of reducing methylene-blue is scarcely perceptible.

A. H.

**Estimation of Saccharose in Mixtures of Maltose, Isomaltose, Dextrin, and in Worts.** By J. JAIS (*Chem. Centr.*, 1893, ii, 893—894; *Zeit. ges. Brauw.*, 16, 349—351).—The author has carefully investigated Meissl's inversion method, and has found that it is perfectly trustworthy.

L. DE K.

**Glycogen.** By S. FRÄNKEL (*Pflüger's Archiv*, 55, 378—379) and J. WEIDENBAUM (*ibid.*, 380—391; compare *Abstr.*, 1893, i, 186).—In reply to Weidenbaum's criticisms on the trichloroacetic acid method of estimating glycogen, the author reaffirms his position, and charges his critic with error, suggesting that he used impure preparations of trichloroacetic acid.

To this, Weidenbaum replies by publishing analyses of his trichloroacetic acid and a number of fresh experiments in which his former conclusions that Fränkel's glycogen contains nitrogen, and that the glycogen is only imperfectly extracted from the tissues by the use of the acid, is fully confirmed.

W. D. H.

**Glycogen.** By W. GULEWITSCH (*Pflüger's Archiv*, 55, 392—393) and by C. PFLÜGER (*ibid.*, 394—401; compare *Abstr.*, 1893, ii, 601).—Gulewitsch points out that Pflüger was not the first to suggest a method for overcoming the difficulties often experienced in the use of Brücke's reagent for the estimation of glycogen. This and certain small points of detail in the methods suggested furnish matter for the polemical portions of the two papers here under review.

W. D. H.



**Estimation of the Acidity of Vinegar.** By L. VANINO (*Zeit. angew. Chem.*, 1893, 676—677).—The author strongly recommends the process originally worked out by Baumann and Kux. 10 grams of the sample of vinegar is mixed with a solution of 4 grams of potassium iodide and 0.8 gram of potassium iodate and introduced by means of a pipette into the bottom part of an ordinary specimen tube, inside which is sealed a small glass cylinder, which contains the alkaline solution of hydrogen peroxide. After standing for at least two hours, the glass is connected with the author's apparatus (*Abstr.*, 1891, 615), which is easier to manipulate than Wagner's azotometer used in Kux's experiments. The two solutions are mixed and the liberated oxygen is finally read off with the usual precautions. The acetic acid is calculated from the volume of gas at N.T.P., or Kux's tables may be used.  
L. DE K.

**Estimation of Malic acid.** By C. MICKO (*Chem. News*, 68, 286).—To facilitate the separation of malic acid in wines by means of lead acetate, the author evaporates 100 c.c. of wine, or 50 c.c. of cider, to a few c.c., sets aside for an hour with 4 or 5 c.c. of binormal sulphuric acid, then, while agitating continuously, gradually mixes in 50 c.c. of strong alcohol and 50 c.c. of ether. After 6 to 10 hours, filtering and washing with ether-alcohol ensue, and the ether and alcohol are subsequently expelled by distillation over a water bath, but finishing off in a vacuum. Chlorides are removed from the residue by cooling it to 50° or 60° and adding the smallest possible excess of freshly prepared silver sulphate and filtering. The filtrate is neutralised with potassium carbonate, evaporated to a small volume, and is ready to be further treated for the separation of malic acid.  
D. A. L.

**Butter Testing.** By E. SPÄTH (*Zeit. angew. Chem.*, 1893, 513—515).—The author uses a kind of weighing flask, the lid and bottom of which are trebly perforated. The bottom, inside, is covered with asbestos. A glass boat, filled one-third with pieces of pumice the size of a pea, is introduced, and the whole is dried for an hour at 105°. The boat is taken out and placed on the balance pan alongside the weighing flask, and weighed. An average lot of butter, weighing about 10 grams, is now put into the boat, and the whole is again weighed. The boat is now placed first on an open water bath for half an hour, then inside an air bath for about two hours at 100°. After cooling, it is put inside the weighing bottle, the whole is re-weighed, and the loss represents the water.

The fat is estimated by placing the whole apparatus inside a Soxhlet tube, and extracting the fat with ether in the usual manner. The salt may be estimated by digesting the insoluble residue in water and estimating the chlorine with silver nitrate. The test analyses show the process to be handy and accurate.  
L. DE K.

**Butter Analysis.** By C. VIOLETTE (*Compt. rend.*, 117, 856—858).—The weight in a vacuum of 1 c.c. of butter at 100° varies from 0.86320 to 0.86425 gram, whilst for margarine the corresponding values are 0.85766—0.85865 gram. The density of a mixture of butter

and margarine is exactly the mean of the densities of its constituents. When cows are fed chiefly on hay, the density of the butter is about 0.86320, whilst if the food consists of grains, pulp, cake, and meal, with very little hay, the density of the butter is about 0.86425. Out of 150 samples of butter, two only, derived from cows highly fed with grains, meal, and cake, gave densities as high as 0.86530 and 0.86540 respectively, whilst one, derived from a cow fed on straw and hay, had a density of 0.86277.

The author has therefore constructed a densimeter, giving all the densities at 100° comprised between those of pure butter on the one hand and margarine on the other, each unit in the fourth decimal place corresponding to a length of 1.4 mm. on the scale. The butter to be examined is heated in a cylindrical copper vessel by means of steam.

For practical purposes, a series of smaller densimeters is used, which allow first of an approximate, and, afterwards, of a more accurate, classification of the butters under examination. Experiments must be made from time to time with average butters from the same district, and from animals fed on various diets. In doubtful cases the butter must be analysed. C. H. B.

**Analysis of Lard.** By C. A. NEUFELD (*Chem. Centr.*, 1893, ii, 778; from *Arch. Hygiene*, 17).—The author comes to the conclusion that neither Hübl's test, nor the silver reaction, are of much use in testing for small quantities of adulterants. L. DE K.

**Estimation of Beef Fat in Lard.** By W. F. K. SROCK (*Analyst*, 19, 2—7).—The author's process is based on the slight solubility of beef stearin in ether at 13°. The requisites are: six 25 c.c. graduated test-mixers fitted with glass stoppers; ether of 0.720 specific gravity; a set of mixtures of pure lard melting at 34—35° with 5, 10, 15, and 20 per cent. of beef stearin melting at 56°; a second set of mixtures of pure lard melting at 39—40° with beef fat melting at 50°.

The melting point of the sample is taken by the capillary tube method 24 hours after the tube has been filled. Suppose the melting point to be at 34°, 3 c.c. of the melted fat is run into one of the test-mixers and dissolved in 21 c.c. of ether, then placed in water at 20—25°. 3 c.c. of each of the first set of mixtures is dissolved in exactly the same way. The five tubes are then cooled down to 13° and allowed to remain at that temperature (particularly towards the last) for 24 hours. The apparent volume of deposit in each tube is then noted, and this will give an immediate clue as to the condition of the sample. The ether is poured off from the tubes as far as possible, and 10 c.c. of fresh ether at 13° is added in each case. The stoppers are inserted, the tubes well shaken, and after the deposit has settled the operation is repeated. The whole contents of the tubes are now transferred to weighed shallow beakers. The ether is carefully run off, and the deposits are dried for 15 minutes at 10°. The beakers are cooled and weighed and the standard weight nearest to that of the sample is used as the factor by which to calculate the beef fat. For samples with a higher melting point, the second set of

mixtures should be used. The actual presence of beef fat must be proved by the microscope. For this purpose, a few particles of the dry residue are placed on a slide, moistened with alcohol, and covered. Very moderate pressure should be applied to the cover, and the slide viewed with a 1-inch objective and the C eye-piece. The presence of beef stearin may often be recognised by the naked eye.

As regards pure lard, the author is enabled to state that no sample melting below 39° gives more than 0.011 gram of ether-washed deposit. A sample melting at 45.8° gave, however, 0.146 gram of deposit. This shows the necessity of having the two sets of standard mixtures and carrying out the analysis by a strict comparison test. Direct experiment has shown that neither cotton oil, palm-nut-kernel oil, nor cocoa-nut oil, interferes with the deposition of the crystals of beef stearin.

L. DE K.

**Furfuraldehyde as a Test for Sesame Oil.** By V. VILLAVECCHIA and G. FABRIS (*Zeit. angew. Chem.*, 1893, 505—506).—The authors recommend the following method for the detection of sesame oil. 0.1 c.c. of a 2 per cent. alcoholic solution of furfuraldehyde is put into a test glass and mixed with 10 c.c. of the sample of oil and 10 c.c. of hydrochloric acid (sp. gr. 1.19). After shaking for half a minute, the mixture is left to itself. If less than 1 per cent. of sesame oil is present, the acid liquid will become carmine-red. In the absence of sesame oil the acid layer will be either colourless or of a dirty-yellow colour. The test may also be carried out as follows:—0.1 c.c. of the furfuraldehyde solution is put into a test glass, mixed with 10 c.c. of oil and 1 c.c. of hydrochloric acid. After thorough shaking, 10 c.c. of chloroform is added to dissolve the oil. In presence of sesame oil, the acid layer will present a fine carmine-red colour, and in its absence there will be either no colour at all or only a trace of green.

By saponifying sesame oil with barium hydroxide and treating the alcoholic extract of the soap with light petroleum, the authors have succeeded in isolating the chromogenic principle.

L. DE K.

**Estimation of Alkaloids by Hulsebosch's Process.** By F. LIECHTIG (*Chem. Centr.*, 1893, ii, 890—891; from *Pharm. Centr. Halle*, 34, 591—593).—The author rejects the process as being utterly untrustworthy, but suggests a few possible improvements in the apparatus, and also recommends liberating the alkaloids by means of lime instead of by sodium hydroxide.

L. DE K.

**Detection of Piperazine in Urine.** By BIESENTHAL (*Chem. Centr.*, 1893, ii, 624—625; from *Therap. Monatsh.*, 1893, 356).—Rörig found (*Therap. Monatsh.*, 1893, 117) that in two cases the addition of picric acid to the urine, after administering piperazine, produced precipitates, which he regarded as albumin. The author considers that these were due to piperazine itself, since this substance, even when diluted 1:20,000 with water, gives a distinct precipitate with picric acid and passes through the organism without change. Usually piperazine shows itself in the urine 3—4 hours after having

been taken; the precipitate produced in such urine with picric acid has the characteristic crystalline form of piperazine picrate, and cannot be mistaken for albumin picrate. The piperazine urine gives none of the reactions of albumin. The identity of the precipitate with piperazine picrate was further shown by decomposing it with hydrochloric acid, removing the picric acid by agitation with ether, and detecting the piperazine by means of a solution of potassium bismuth iodide. The presence of piperazine could even be detected in the urine itself by the use of this reagent. In order to detect albumin along with piperazine in urine, acetic acid may be employed; this coagulates the albumin on heating, and the coagulum does not redissolve, whereas the precipitate of piperazine picrate disappears on heating and reappears on cooling.

A. H.

**Test for Cocaine.** By SCHÄRGEN (*Chem. Centr.*, 1893, ii, 888; from *Schweiz. Woch. Pharm.*, 31, 341—343).—A few centigrams of the alkaloid is dissolved in a drop of water and a drop of sulphuric acid. On adding to the colourless solution a drop of a solution of potassium chromate, or dichromate, a rapidly-vanishing precipitate is obtained. On warming, the liquid turns green and gives fumes resembling those of benzoic acid. Cocaine is distinguished from morphine by its insolubility in cold solutions of fixed alkalis.

L. DE K.

**Detection of "Saccharin" in Wines and Beers.** By E. SPAETH (*Zeit. angew. Chem.*, 1893, 579—581).—To detect saccharin in wines or cordials, the sample is mixed with purified sand, evaporated to about 10—20 c.c., acidified with a few c.c. of phosphoric acid, and extracted, at a gentle heat, with a mixture of equal parts of ether and light petroleum (b. p. 60°). After filtering through asbestos, the mass is again extracted until the filtrate measures about 200—250 c.c. After distilling off the solvent, the residue is taken up with a very weak solution of sodium carbonate and tasted. A sweet taste points to the presence of "saccharin," the amount of which may be ascertained as usual by a fusion with nitre and an estimation of the sulphate so produced.

When applying the process to beers, the bitter principles of the hops must be first removed by adding a few crystals of copper nitrate. The liquid need not be filtered.

L. DE K.

**Reaction of Indoles.** By A. ANGELI (*Gazzetta*, 23, ii, 102—103).—On melting a trace of an indole or indolecarboxylic acid with dehydrated oxalic acid in a test tube, a beautiful coloration is produced, and can be dissolved in acetic acid. Indole and its aliphatic derivatives give a magenta colour, whilst  $\alpha$ -phenylindole yields a violet colouring matter.

W. J. P.

**Process for the Full Analysis of Root Crops.** By A. v. ASBÖRN (*Chem. Zeit.*, 17, 725—726).—The author recommends the following process for the analysis of potatoes:—The substance is cut into thin slices, and about 8 grams of the sample is dried, first at 50°, and then at 110°. The loss represents the moisture. If the

temperature is raised too rapidly, the starch gelatinises, and is then very difficult to dry. The dried substance is incinerated, and the mineral matter weighed. For the estimation of the other constituents, about five potatoes are cut up, partially dried at 50°, reduced to powder, and then finely ground; the flour is then subjected to analysis. The remaining moisture is determined by drying at 110°, and the total nitrogen is determined by Kjehldahl's process as modified by the author. [The substance is boiled with sulphuric acid and copper sulphate, potassium permanganate being only used in extreme cases; the liquid is distilled with aqueous soda containing Rochelle salt, and the ammonia is then titrated.—ABTRACTOR.] The fatty matter is estimated by exhausting 10 grams of the flour with ether in a Soxhlet's tube, the residue being exposed to the air until all the ether has gone off. About 2 grams of it is taken for the estimation of the starch and dextrin by the author's baryta method (Abstr., 1887, 868), but it is necessary to redetermine the moisture and make due correction for any alteration. The minor constituents are estimated by triturating 5 grams of the flour with cold water, and collecting the insoluble mass on a weighed filter. After drying, a portion of it is used for a nitrogen estimation (insoluble proteids). The solution is evaporated on the water bath, and the residue finally dried for three hours over sulphuric acid in a vacuum; this gives the total soluble matter; it is then treated with water, and any proteid matter which has coagulated is collected on a weighed filter, dried, and weighed.

The filtrate is concentrated to a syrup and mixed with twice its volume of alcohol. The precipitate is washed with alcohol, dissolved in water, and titrated by means of baryta, which gives the dextrin. The alcoholic solution is evaporated in a platinum dish, and the residue, after drying in a vacuum, is weighed; this gives the sugar and amido-acids. The sugar may be estimated by Fehling's solution, and the amido-acids are then taken by difference; they may, however, also be estimated directly by deducting from the total nitrogen the nitrogen due to the proteids, and calculating the difference to asparagine, which contains 21.97 per cent. of nitrogen. By taking the sum of the soluble proteid, dextrin, and asparagine, and deducting this from the matter soluble in water, the difference gives the colouring matters and gummy substances.

In conclusion, the author gives the details of an analysis of a variety of red potato, popularly known as the Zulu-King. Not a trace of sugar was found. As the result is very favourable, the cultivation of this crop on the large scale is much to be recommended.

L. DE K.

**The Ferrocyanide Test for Urine.** By J. P. KARPLUS (*Chem. Centr.*, 1893, ii, 496; from *Centr. klin. Med.*, 14, 577).—See this vol., ii, 107.

**Estimation of Proteids and Extractives in Cow's and Human Milk.** By I. MUNK (*Virchow's Archiv*, 134, 519—540).—See this vol., ii, 106.

## General and Physical Chemistry.

**Absorption Spectra of Solutions of the Chromoxalates of the Blue Series.** By G. MAGNANINI and T. BENTIVOGLIO (*Gazzetta*, 23, ii, 444—451; compare Lapraik, *Abstr.*, 1893, ii, 313).—Ostwald (*Abstr.*, 1892, 1137), from a study of a number of salts, concluded that the similar absorption possessed by very dilute solutions of salts containing one coloured ion in common is due to the complete electrolytic dissociation of the salts, the coefficient of absorption being proportional to the number of coloured ions in solution. Ostwald examined very dilute solutions of the chromoxalates, amongst others, and found their absorption coefficients to be proportional merely to the concentrations.

The authors have measured the absorption of solutions of the chromoxalates of potassium, sodium, and ammonium, and confirm Ostwald's results. They find further, however, that the absorption coefficients are also proportional to the concentration in very concentrated solutions (20—25 per cent.), in which the dissociation is small. The absorption in concentrated solutions thus follows the same law as that in dilute highly dissociated solutions. The absorption coefficient is not altered by the addition of a salt containing the same metallic ion as the chromoxalate, although the dissociation of the latter is so greatly reduced by the over-pressure of the metallic ion. The authors conclude that the absorption of the chromoxalates is absolutely independent of the extent of their electrolytic dissociation.

W. J. P.

**Comparative Experiments on the E.M.F. of the Clark Standard Cell.** By K. KÄHLE (*Ann. Phys. Chem.*, [2], 51, 174—202).—The experiments detailed in this paper were made with the object of ascertaining the effects which change of form, purity of material, age, and temperature have on the E.M.F. of the Clark standard cell. The H-form devised by Lord Rayleigh, the form proposed by Feussner, and that adopted by the Board of Trade were compared with one another. The results show that the H-cell is far superior to the other two, both in the ease with which it can at any time be reproduced of constant E.M.F. and in the fact that impurities and disturbing influences have less effect on its constancy, so that the variation of its E.M.F. from the normal value can with little difficulty be reduced to 0.0001 volt. Greater changes than this were not observed in cells which were often compared with one another during the course of 1½ years. In the effect which temperature has on this cell, it is also to be placed before the others. The author finds that a knowledge of the temperature coefficients of the Feussner and Board of Trade cells is misleading, as the E.M.F. calculated by their means does not agree with that actually observed. On the other hand, as long as sudden changes of temperature are avoided, the value of the E.M.F. for the H-cell can be calculated for different

temperatures to within 0.0001 volt, and even with sudden temperature changes to within 0.001 volt. The coefficient for temperatures between 10° and 30° was found to be  $-0.000814 - 0.000007(t-15)$ .

The constancy discovered in the E.M.F. of the above form of the Clark standard cell leads the author to propose its adoption for the purpose of defining the unit of electromotive force. He condemns the form of cell adopted by the Board of Trade as not sufficiently fulfilling the requirements of a standard.

H. C.

**Instructions for the Preparation of the Clark Standard Cell.** By K. KAHLE (*Ann. Phys. Chem.*, [2], 51, 203—211).—Instructions are given for the preparation of the Clark standard cell in the H-form, which the author finds to be the most suitable (see preceding abstract). The principal points requiring attention are that the mercury serving as the positive electrode should be as free as possible from impurity, that the whole of the active surface of the electrodes should be kept in contact with a solution of zinc sulphate, that is maintained always in a concentrated condition by the presence of zinc sulphate crystals, and that the zinc sulphate should contain no free acid.

H. C.

**Electrical Conductivity of some Solutions of Salts, especially of Calcium, Strontium, and Barium.** By A. C. MAC GREGORY (*Ann. Phys. Chem.*, [2], 51, 126—139).—The author has determined the conductivities of solutions of calcium chloride, nitrate, sulphate, and acetate; strontium chloride, nitrate, and acetate; barium and silver acetates; and potassium oxalate. The results are given in tabular and curve form. The curves for the molecular conductivities are in general of a perfectly regular character, and show little tendency, even with the most dilute solutions, to a departure from their usually rectilinear character. Silver acetate shows, however, a change in curvature in dilute solutions, for which no cause can as yet be assigned.

H. C.

**Electrical Conductivity of Solutions of Salts of Organic Acids in presence of Boric Acid.** By G. MAGNANINI and T. BENTIVOGLIO (*Gazzetta*, 23, ii, 451—457).—The present paper deals with the influence of boric acid on the electrical conductivity of solutions of salts of various organic acids, the object being to determine whether Magnanini's method (*Abstr.*, 1893, ii, 506) for detecting hydroxyl in organic acids could be applied to solutions of the salts. The behaviour of solutions of sodium acetate, citrate, and salicylate, potassium and sodium tartrates, and calcium lactate was examined. The conclusion is deduced that the results obtained with solutions of the salts are not so certain as with those of the acids.

W. J. P.

**Densities of Saturated Vapours and their Relation to the Laws of Solidification and Vaporisation of Solvents.** By F. M. RAOULT (*Compt. rend.*, 117, 833—837).—The author, in conjunction with Recoura, has shown that if  $d'$  is the density of a satu-

rated vapour determined experimentally, and  $d$  is its theoretical value,

$$\frac{d'}{d} = \frac{f - f'}{f} \frac{100}{P} \frac{M_1}{M},$$

where  $f$  and  $f'$  are the vapour pressures of the solvent and the solution,  $P$  the weight of substance dissolved in 100 grams of solvent, and  $M$  and  $M_1$  the molecular weights of solvent and dissolved substance. Since Guldberg has shown that there is a relationship between the depression of the freezing point and that of the vapour tension, the above relation may, in accordance with well-known principles, be transformed into

$$\frac{d'}{d} = 1.988 \frac{f - f'}{fC} \frac{T^2}{L_1 M},$$

where  $C$  is the reduction of the freezing point,  $L_1$  the latent heat of fusion, and  $T$  the absolute temperature. The relationship holds for any dilute solution, and the author shows that it is in general keeping with the theory of dilute solutions, and is verified by experiment.  
H. C.

**Vapour Tension Measurements.** By G. W. A. KAHLBAUM (*Zeit. physikal. Chem.*, 13, 14—55).—This paper gives the results of a large number of experiments made to test the concordance or disagreement of the statical and dynamical methods of determining vapour pressures. The first liquids employed were water and mercury, in which the author's dynamical measurements agreed well with the statical numbers given by Regnault, by Hertz, and by Ramsay and Young. As Landolt's statical determinations in the case of the first five fatty acids did not agree with the author's previous dynamical determinations, Landolt's work was repeated. Two unavoidable sources of error are considered to affect statical measurement, namely, the impossibility of placing the liquid perfectly free from air in the vacuum chamber of the barometer, and the impossibility of obtaining the liquid absolutely dry; these the author believes to be the cause of the previously obtained *regular* variation between the results of the two methods. As a result of his determinations, he concludes that the "statical and dynamical methods of vapour tension measurement give concordant results." The differences previously supposed to exist had been regarded as due to the fact that in the statical method it is only the cohesion of the surface molecules which is loosened, whilst in the dynamical method the cohesion of all the molecules, including those in the midst of the liquid, has to be overcome. The author considers, however, that, owing to the presence of air and other particles, surfaces do exist in the midst of the liquid at which evaporation takes place, so that in both methods it is only the cohesion of surface molecules which is concerned. The results of a large number of measurements with different liquids are tabulated, all done by the dynamical method to avoid the above-mentioned inevitable causes of error. Tables are given for the vapour pressures at different temperatures, and of the boiling points at different pressures in the case of the first ten normal fatty acids,



for isobutyric, isovaleric, and isocaproic acids, and for mixtures with water and among themselves of some of these liquids. In no case, however, is the pressure higher than 75 mm., the majority of the liquids being observed at pressures varying from 0 to 60 mm. The paper closes with a statement that Dalton's law has as little validity for the homologous fatty acids as for the fatty alcohols, which is contrary to the opinion held by G. C. Schmidt (Abstr., 1891, 969; 1892, 396).  
L. M. J.

**Dissociation Constants of Water and Hydrocyanic acid.** By J. J. VAN LAAR (*Zeit. physikal. Chem.*, 12, 742—750).—From the experiments of Shields, Bredig, and others the author calculates the following dissociation constants:—

Acetic acid . . . . .	$k = 1800.00 \times 10^{-4}$
Hydrocyanic acid . . . .	$k = 3.1 \times 10^{-6}$
Aniline . . . . .	$k = 1.1 \times 10^{-8}$
Phenol . . . . .	$k = 0.42 \times 10^{-8}$
Water . . . . .	$k = 0.70 \times 10^{-14}$

It will be seen that hydrocyanic acid, which is 600 times weaker than acetic acid, is more than four million times stronger than water.

H. C.

**Composition of Saline Solutions deduced from their Indices of Refraction.** By P. BARY (*Compt. rend.*, 118, 71—73).—In a former paper (Abstr., 1892, 929) the author has shown that the presence of hydrates in aqueous solutions may be deduced from the refractive indices of such solutions. The experiments recorded applied only to concentrated solutions, but the method has now been adapted to the examination of solutions of considerable dilution. The refractive indices of dilute solutions of potassium chloride are found to be strictly proportional to the amounts of salt contained in these solutions, and afford no indication of the occurrence of electrolytic dissociation.

H. C.

**How the Theory of Solutions Arose.** By J. H. VAN'T HOFF (*Ber.*, 27, 6—19).—In this account of an address delivered to the German Chemical Society, the author first shows how from a consideration of the relations between constitution and chemical properties he was led to consider the rate of chemical actions, the equilibrium of opposed reactions, the thermodynamical basis of the equilibrium, and finally the general problem of affinity. The first affinity problem he investigated was the simple one of the attraction of water by salts with water of crystallisation, and while studying this subject he became acquainted with Pfeffer's osmotic researches. A thermodynamical consideration of the two phenomena jointly led to the conception of osmotic pressure in solutions as the analogue of gaseous pressure in gases, and enabled him to show how substances in dilute solution obeyed laws perfectly analogous to the ordinary gas laws, namely those of Boyle, Charles, and Avogadro.

He next deals with the theory of dilute solutions, and deduces from the osmotic pressure (1) the lowering of the vapour pressure,

(2) the elevation of the boiling point, and (3) the depression of the freezing point.

The third section of his address is occupied with the deviations from the simple laws. First, he discusses abnormally small freezing point depressions, then those that are abnormally large, and shows how the latter are accounted for by Arrhenius' hypothesis of electrolytic dissociation. Lastly, he calculates the amount of ionisation of pure water from experiments on the rate of catalysis of ethylic acetate, the minimum velocity predicted by the dissociation theory being experimentally verified. J. W.

**The Hydrate Theory.** By S. U. PICKERING (*Ber.*, 27, 30—31).—In answer to W. Meyerhoffer (this vol., ii, 9), the author, whilst admitting the obvious identity of freezing point and solubility curves, states that it does not, therefore, follow that changes of curvature in them can be caused by changes in the nature of the crystallising substance only, but they can be caused by changes in the constitution of the liquid also, and the whole gist of the present hydrate theory lies in recognising the existence of such changes. S. U. P.

**Cryoscopic Molecular Weight Determinations in Benzene.** By K. AUWERS (*Zeit. physikal. Chem.*, 12, 669—722).—Certain irregularities which have been noticed in the cryoscopic behaviour of benzene solutions have induced the author to make a large number of different observations with a number of such solutions, chiefly with the view of ascertaining the suitability of benzene as a solvent in molecular weight determinations. Substances containing a hydroxyl group, the behaviour of which in benzene Raoult pronounced irregular, are found to behave in the normal manner provided the solutions taken are sufficiently dilute. The phenols in fairly concentrated solution even show this normal behaviour, but the aliphatic hydroxyl compounds give abnormal depressions in concentrated benzene solutions. This behaviour may in certain cases serve as a guide in establishing the constitution of compounds which are supposed to belong to this class. All acids hitherto examined give, in benzene solutions of medium concentration, a depression corresponding with about double the ordinarily-accepted molecular weight. This behaviour also serves as a most important guide in questions of constitution. H. C.

**Solutions of Sodium Silicates and Influence of Time on their Constitution.** By F. KOHLRAUSCH (*Zeit. physikal. Chem.*, 12, 773—791).—See Abstr., 1893, ii, 166. H. C.

**Action of Hydrogen Chloride on Ethylic Alcohol.** By J. C. CAMM (*Zeit. physikal. Chem.*, 12, 751—761).—The action of hydrogen chloride on ethylic alcohol was studied as a time reaction. The fact that the reaction in question is a reversible one was first established. The influence of temperature is very considerable. There is practically no action at 15°, but as the temperature rises the rate of decomposition rapidly increases. The following table, which applies

to a mixture of 100 equivalents of alcohol with 31.2 equivalents of hydrogen chloride, gives the percentage decomposition of the hydrogen chloride in 27 hours at different temperatures.

Temperature .....	40°	60°	80°	90°
Per cent. HCl decomposed..	6.77	32.34	71.32	90.64

Excess of alcohol exercises a retarding influence, and the same thing applies, but in smaller degree, to the influence of ethylic chloride. The Guldberg-Waage law applies to the action provided the quantity of alcohol taken is sufficient to dissolve the ethylic chloride formed, and that separation of the solution into two layers does not take place.  
H. C.

**New Apparatus for Sublimation.** By G. ODDO (*Gazzetta*, 23, ii, 313—314).—The following method gives good results in the purification of substances by sublimation. The substance is placed in a small beaker, which is fitted into a hole in a piece of asbestos card standing on a ring support; a beaker, in which the sublimate collects, is then inverted over this, and a third beaker is placed over the second. The beaker containing the substance is heated by radiation from a second asbestos disc placed below it, to which heat is applied by means of a bunsen burner.  
W. J. P.

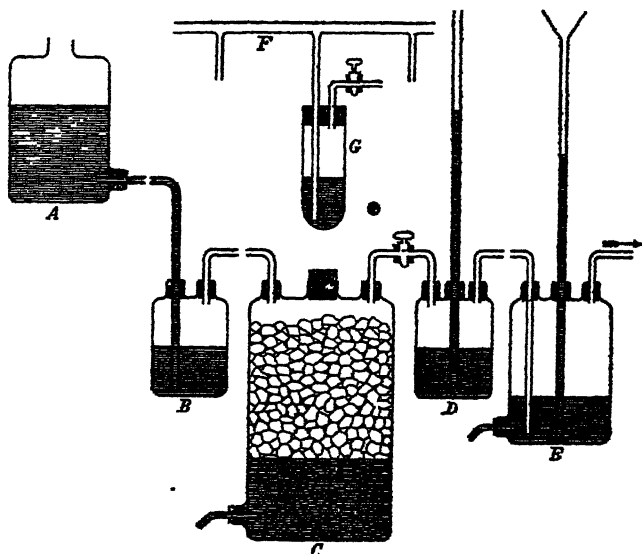
**Condensers.** By J. WALTER (*J. pr. Chem.*, [2], 49, 44—48).—Further improvements in the author's form of condenser (*Abstr.*, 1887, 105) are depicted.  
A. G. B.

**Critical Studies in Preparation Exercises.** By S. P. L. SÖRENSEN (*Zeit. anorg. Chem.*, 5, 354—373).—Considering that for purposes of preparation exercises, a more critical examination of the modes of preparation of inorganic substances is required than is found in available text books, the author has investigated the methods for preparing pure nickel and cobalt compounds. He describes modified methods, for the details of which the original must be consulted, and gives a critical review of the methods which have been proposed by successive investigators, but omits mention of the method of Mond, Langer and Quincke (*Trans.*, 1890, 750) of obtaining absolutely pure nickel by means of nickel carbonyl which has proved to be so successful.  
L. T. T

## Inorganic Chemistry.

**Hydrogen Sulphide Apparatus.** By F. W. KÜSTER (*J. pr. Chem.*, [2], 48, 595—598). The bottle A (5 litres) is placed at such a height above the bottle B (3 litres) as will serve to supply the *plus* pressure required in the apparatus, and receives the acid (2 vols. of common hydrochloric acid and 1 vol. of water) which is to evolve

hydrogen sulphide from the large pieces of ferrous sulphide in the bottle C (10 litres). The trap D serves to prevent the regurgitation of the aqueous hydrogen sulphide in E. Inasmuch as the water in this last-mentioned bottle is saturated with the gas at the pressure of the apparatus, it is always in the best possible condition for use



when drawn off by the tap in the bottom of the bottle. The tubes connecting A, B, and C should be drawn out at the ends to allow of only a slow passage of the acid. When the gas is drawn off from the cock of the small washing bottle G, attached to the general supply tube F, the acid falls from A, through B into C, and is driven back when the exit is again closed. Inasmuch as C may be made to hold enough ferrous sulphide to yield 10,000 litres of gas, it is only necessary to see that A is filled with acid, and C emptied of ferrous chloride solution, every morning. A. G. B.

**Combination of Hydrogen and Selenium in a Vessel not uniformly heated.** By H. PÉLABON (*Compt. rend.*, 118, 142—144). Ditte has shown that when one part of the extremities of a tube containing selenium and hydrogen is heated above  $300^{\circ}$ , crystals of selenium appear after a time at another part of the tube, where the temperature is very near the melting point of selenium (about  $270^{\circ}$ ). This particular temperature the author distinguishes as  $\theta$ . Experiments show that when no part of the tube is at a temperature lower than  $\theta$ , the final composition of the mixture is that corresponding with the temperature of the coolest part of the tube. In all cases the excess of selenium at the close of the experiment is found at the coldest extremity of the tube.

When the hottest part of the tube is at a temperature higher than, and the coldest part at a temperature lower than  $\theta$ , the final composition of the mixture is independent of the extreme temperatures of the tube. The excess of selenium condenses at the point where the temperature has the value  $\theta$ . It would seem that the formation of hydrogen selenide in the hot parts of the tube ought to take place more rapidly than its destruction in the cold parts, and if, in the preceding experiments, the tubes are suddenly cooled before the whole of the selenium has disappeared from the hottest part of the tube, the composition of the gaseous mixture practically corresponds with the highest temperature of the tube.

When no part of the tube is at a temperature as high as  $\theta$ , the final composition of the gaseous mixture is that which corresponds to the highest temperature of any part of the tube. C. H. B.

**Formation of Hyponitrous acid.** By S. TANATAR (*J. Russ. Chem. Soc.*, 25, 342—345).—When solid hydroxylamine chloride and potassium nitrite are mixed in equivalent proportions, there is a violent action, nitrous oxide being evolved. In dilute solution (1 part  $\text{NH}_3\text{O}$ ,  $\text{HCl}$  to 20 parts water), the reaction takes place, slowly, and in the course of a few hours silver nitrate gives a precipitate of silver chloride, coloured yellow by silver hyponitrite, which may be obtained pure by dissolving it out with nitric acid, and precipitating the solution with sodium acetate. Better results are obtained by adding lime (1 mol.) to the moderately strong solution of potassium nitrite (1 mol.), then the hydroxylamine hydrochloride, heating to  $50^\circ$ , allowing the mixture to remain for a day or two at the ordinary temperature. The filtrate from the excess of lime is acidified with acetic acid, silver nitrate is added, and the hyponitrite separated from the silver chloride as described above. The author recommends this as the best method of obtaining the hyponitrites. J. W.

**The Reaction between Hydroxylamine Hydrochloride and Sodium Nitrite.** By S. TANATAR (*Ber.*, 27, 187; see preceding abstract). The reaction takes place with difficulty in alkaline solution and in the presence of magnesia, zinc oxide, cadmium oxide, and calcium carbonate. If the acid solution of hydroxylamine hydrochloride is first neutralised it does not react with sodium nitrite. The violent reaction between solid hydroxylamine hydrochloride and sodium nitrite does not take place in the presence of lime, magnesia, or zinc oxide. E. C. R.

**Preparation of Phosphorus from the Phosphates of the Alkalis and Alkaline Earths by means of Aluminium: Action of Aluminium on Sulphates and Chlorides.** By A. ROSSEL and L. FRANK (*Ber.*, 27, 52—55).—When sodium metaphosphate is heated with aluminium in a current of hydrogen, 28—31 per cent. of the phosphorus distils over, and a residue is obtained consisting of alumina, sodium aluminate, and aluminium phosphide. All the phosphates of calcium and magnesium, when heated with aluminium,

yield phosphorus. *Aluminium phosphide*.  $\text{AlP}_3$ , is obtained by heating aluminium in phosphorus vapour, and then heating the product until phosphorus ceases to come off. It is a grey, crystalline powder.

The whole of the phosphorus in the phosphates may be obtained by adding silica to the mixture in the proportions represented by the equation  $3\text{Ca}(\text{PO}_3)_2 + 10\text{Al} + 3\text{SiO}_2 = 3\text{CaSiO}_3 + 5\text{Al}_2\text{O}_3 + 3\text{P}_4$ .

When a mixture of calcium metaphosphate and calcium sulphate was heated with aluminium, a violent explosion ensued. The authors find that this is due to the sulphate; barium sulphate or calcium sulphate, when heated with aluminium, act with explosive violence, and sulphur is set free. The chlorides are also decomposed by aluminium at a high temperature.

E. C. R.

**Alkali Orthophosphates.** By L. STAUDENMAIER (*Zeit. anorg. Chem.*, 5, 383—396).—With the intention of determining whether two possible isomeric dipotassium disodium pyrophosphates (one symmetrical, the other unsymmetrical) exist, the author attempted to prepare dipotassium phosphate,  $\text{K}_2\text{HPO}_4$ . Not obtaining satisfactory results, and finding the literature on the subject very conflicting, he has carefully investigated the question. All attempts to prepare dipotassium phosphate proved futile, and the statements of Thomson, Graham, Berzelius, and Mitscherlich, and of chemical text-books in regard to this substance are incorrect.

In the course of experiments to prepare dipotassium phosphate by the action of monopotassium phosphate ( $\text{KH}_2\text{PO}_4$ ) on sodium carbonate, rhombic crystals of 1—2 mm. in length were obtained; these are very deliquescent, and exceedingly soluble in water, from which solution, however, the monophosphate crystallises out. The crystals on analysis were found to correspond exactly with the formula  $\text{K}_5\text{H}_4(\text{PO}_4)_3\cdot\text{H}_2\text{O}$ . This salt is alkaline in reaction, and on ignition leaves a mixture of potassium pyro- and meta-phosphates. By substituting potassium hydroxide for potassium carbonate, using a rather larger proportion of this, and treating the product in a similar way, the author obtained a salt of the formula  $\text{K}_7\text{H}_5(\text{PO}_4)_3\cdot 2\text{H}_2\text{O}$ , forming crystals very closely resembling those of the compound just described. It differs from them, however, in that if left on a porous plate exposed to the air, it deliquesces and sinks entirely into the plate, whilst under like conditions the salt  $\text{K}_5\text{H}_4(\text{PO}_4)_3\cdot\text{H}_2\text{O}$  always leaves some monopotassium phosphate on the plate. The author was unable to isolate any potassium salt of a more basic character, even when a much larger proportion of base was used.

The author has also obtained per-acid phosphates of the alkalis. The *potassium* salt,  $\text{KH}_5(\text{PO}_4)_3$ , was obtained by mixing, in solution, monopotassium phosphate with phosphoric acid, in molecular proportion, evaporating the solution to a small bulk, and allowing it to remain. It crystallises in long needles, has a very strong acid taste, melts at  $127^\circ$ , and then forms a viscid mass which does not re-solidify. On further heating, water is first evolved, then phosphoric acid, and potassium metaphosphate is left. Alcohol causes the crystals to become opaque, by dissolving the acid and leaving monopotassium phosphate. The

ammonium salt.  $(\text{NH}_4)_3\text{H}_2(\text{PO}_4)_2$  closely resembles the potassium salt in form and properties. The sodium salt is isomorphous with the potassium salt, and melts at  $131^\circ$ .  
L. T. T.

**Action of Sodium on Water.** By M. ROSENFELD (*J. pr. Chem.*, [2], 48, 599—601).—The explosion which occurs when water is poured on to sodium has been supposed to be due to the formation of sodium peroxide, which subsequently decomposes, and thus produces an explosive mixture of hydrogen with oxygen. It is now shown that no oxygen can be detected in the gas obtained by passing steam over sodium. The author concludes that the explosion is due to the decomposition of sodium hydride, which may be expected to be formed when sodium acts on water; the conclusion is supported by the observation that the explosion takes place in the centre of the sodium. When steam is passed over sodium no hydride is formed, because the tension of the hydrogen is kept very low by the current of steam. A safe and rapid method for obtaining hydrogen is to pass steam through an iron box, with an air-tight lid, containing sodium. If the passage of steam be continued until no more hydrogen is evolved, and if the quantity of gas be measured, a calculable weight of sodium hydroxide will remain in the box, and will serve for the preparation of a standard solution.  
A. G. B.

**Decomposition of Sodium Dioxide by Aluminium.** By A. ROSSER and L. FRANK (*Ber.*, 27, 55).—When a mixture of sodium dioxide and aluminium powder is exposed to damp air, spontaneous composition ensues. If the mixture is moistened, a very high temperature is produced.  
E. C. R.

**Hydrates of Lithium Chloride and Bromide.** By A. BUGORODSKY (*J. Russ. Chem. Soc.*, 25, 316—341).—The author describes the preparation and properties of the following hydrates:—



J. W.

**Action of Mercuric Chloride on Metallic Silver.** By H. C. JONES (*J. Soc. Chem. Ind.*, 12, 983—988).—By the action of a solution of mercuric chloride, the metallic silver of a silver photographic image is changed into a white substance hitherto supposed to be a mixture of mercurous and silver chlorides; the author has investigated the matter, and now regards this substance as a compound of the composition  $\text{HgAgCl}$ .

Mercuric chloride acts but slowly on silver, and therefore many methods for preparing this substance were tried; finally the following was adopted. A considerable excess of mercuric chloride, made into a thin paste with water, is mixed with pulverulent silver, agitated frequently, and occasionally ground in a mortar, during two or three weeks, then, after heating from 12 to 20 hours in a flask in a water bath, is mixed with a considerable quantity of water in which most of the excess of mercuric chloride is allowed to settle, whilst the turbid supernatant liquid is poured off, and by repeating the operation most of the

preparation is obtained in suspension and soon settles out. The preparation on heating loses mercurous chloride by volatilisation, and silver chloride remains behind: if, however, any free silver be present it is converted into chloride, and a corresponding quantity of mercury volatilises. With excess of mercury, the reverse takes place, inasmuch as it removes some of the chlorine that would otherwise remain as silver chloride.

The sp. gr. of silver chloride is 5.590; of mercurous chloride, 7.256; a difference which would permit of their separation when settling from suspension in water: it has been found, however, that the preparation, when allowed to settle in a long tube filled with water, so as to form a 7-inch layer, shows no signs of separation, material from the top and from the bottom of the layer giving exactly the same numbers on analysis. Moreover, calculation shows that a mixture of equivalent proportions of the two chlorides would have a sp. gr. of 6.626, whereas the sp. gr. of the preparation is 6.505. This substance is slowly affected by light, especially when moist; it also gives the following reactions:—With hydrochloric acid, it yields silver chloride, mercuric chloride, and mercury; with ferrous oxalate, it is completely reduced; with the alkalis, a partial exchange of oxygen for chlorine ensues; with ammonium chloride, potassium chloride, potassium cyanide, or sodium thiosulphate, one-third of both silver and mercury remains as a metallic residue, the rest dissolves; with sodium sulphite, one-half the silver and one-third of the mercury remains undissolved as a metallic residue; with potassium silver cyanide, all the silver is deposited as metal; with ammonia, substituted ammonium salts are obtained containing both silver and mercury. The author considers that he adduces sufficient evidence to support his view that the substance in question is not a mere mixture of mercurous and silver chlorides, but is a compound of the composition  $\text{HgAgCl}_2$ ; for, only the first three of the above reactions could be explained on the mixture assumption, whilst all of them can be explained by use of the author's formula. Incidentally it is noted that mercuric chloride has been observed to act on the mixed metallic residues obtained in the above reactions somewhat in this way:  $\text{HgAg} + 2\text{HgCl}_2 = \text{Hg}_3\text{AgCl}_4$ .  
D. A. L.

**Molecular Weight of Mercurous Nitrate determined by the Cryoscopic Method.** By F. CANZONERI (*Gazzetta*, 23, ii, 432—437).—The author has determined the depression of the freezing point of dilute nitric acid by mercurous nitrate, and concludes that the salt has the molecular formula  $\text{Hg}_2(\text{NO}_3)_2$ . The freezing points of only two solutions of the salt were determined.  
W. J. P.

**Ceric Dichromate. The Separation of Cerium from Lanthanum and Didymium.** By G. BRICOUT (*Compt. rend.*, 118, 145—146).—When an electric current of 2.5 to 3 volts. is passed through the slightly acid solution, obtained by dissolving cerous carbonate in chromic acid, a large positive electrode being used, small, brilliant, orange-red crystals of ceric dichromate,  $\text{CeO}_3 \cdot 2\text{CrO}_3 \cdot 2\text{H}_2\text{O}$ , separate on the positive electrode. This compound is insoluble in



water, but dissolves in acids. It is slightly decomposed by cold water, and when boiled with water is first converted into yellow ceric chromate, and eventually into hydrated ceric oxide.

Lanthanum and didymium form no higher oxides, and hence, under similar conditions, give no deposit on the positive electrode. Ceric dichromate, precipitated in the manner described, from solutions containing lanthanum and didymium, is quite free from these elements, and can readily be dissolved in hydrochloric acid and precipitated in the form of oxalate.

C. H. B.

**Electrolysis of Ferrous Sulphate.** By M. TICHVINSKY (*J. Russ. Chem. Soc.*, 25, 311—315).—When a 30 per cent. solution of ferrous sulphate is electrolysed between iron electrodes by a very weak current in the dark, a solution is obtained in the course of a month or two which differs considerably from the ordinary solutions of ferrous salts. Its colour is more intensely green, somewhat like that of nickel sulphate, and on exposure to light, it deposits a green solid, which may be preserved for an indefinite period if air is excluded. Analysis of the solution showed it to contain twice as much iron for a given quantity of sulphuric acid as is contained in ferrous sulphate. It therefore probably contains the basic salt  $\text{FeSO}_4 \cdot \text{FeO}$ , which decomposes on exposure to light with deposition of  $\text{Fe}(\text{OH})_2$ , coloured green by some ferrous sulphate carried down along with it. This appears likely, because the precipitate on washing becomes much paler.

J. W.

**Action of Ferric Salts on Iodides.** By K. SEUBERT (*Zeit. anorg. Chem.*, 5, 334—338).—This paper forms a historical introduction to the paper of Seubert and Dorrer (see next Abstract). The author points out that this reaction is generally represented by the equation  $\text{Fe}_2\text{Cl}_6 + 6\text{MI} = 2\text{FeI}_2 + 6\text{MCl} + \text{I}_2$ , or  $\text{Fe}_2\text{Cl}_6 + 2\text{MI} = 2\text{FeCl}_2 + 2\text{MCl} + \text{I}_2$ , but that neither of these represents the true facts. For, whilst in strong solutions, and with a large excess of iodide, the theoretical quantity of iodine may be liberated, in general less than this quantity is set free, the quantity in weak solutions showing a considerable deficiency. Very weak solutions of ferrous chloride even absorb iodine with the formation of some ferric salt. It is thus clear that this reaction is a reversible one.

L. T. T.

**Action of Ferric Chloride on Potassium Iodide and on Hydriodic acid.** Part I. By K. SEUBERT and A. DORRER (*Zeit. anorg. Chem.*, 5, 339—353).—In this part of the paper, the results of the action of neutral solutions of ferric chloride on potassium iodide are described. Deci-molecular solutions were used ( $\text{FeCl}_3$  being considered as the molecule of ferric chloride), and quantities of 10 c.c., or multiples thereof, taken so as to correspond, on the one hand, with 1 to 50 mols. of potassium iodide to 1 mol. of ferric chloride, and on the other with 1 to 10 mols. of ferric chloride to 1 mol. of potassium iodide. The influence of time and of dilution on the

reaction was also studied. The results are given in a series of full tables and curves, which may be thus summarized.

1. *Influence of time on the reaction.*—In order to allow the progress of the reaction to be followed, the mixed solutions were, in these series, always diluted to 100 c.c. The progress of the reaction, where the two substances are used in molecular proportion, is most rapid in the first quarter of an hour, by the end of which time about 28 per cent. of the theoretical quantity of iodine has been set free, and then rapidly decreases until after five or six hours (at which time 50–51 per cent. of the theoretical iodine has been liberated), further action is exceedingly slow. At the end of 46 hours, 60 per cent. of the theoretically possible iodine has been set free. The reaction, when the molecular proportions are equal, does not seem to proceed much beyond this point; but when unequal molecular proportions are used, the progress of the reaction is quicker, the end state of equilibrium is sooner reached, and the total quantity of iodine liberated is greater the greater the excess of either reagent employed, excess of potassium iodide exerting, however, a somewhat greater influence than excess of ferric chloride.

2. *Influence of the mass of the two reagents on the reaction.*—As already seen, the total quantity of iodine liberated by the mutual action of potassium iodide and ferric chloride in molecular proportion is below 60 per cent. of that required by the theoretical equation. Increase of either reagent augments this quantity. At first, increase of potassium iodide has more effect than a similar increase of ferric chloride. But, after a time, the effect of increasing the iodide ceases, and about 96–97 per cent. of the theoretical iodine is the most that can be liberated in this way. With excess of ferric chloride, on the other hand, the influence is at first less, but continues more regularly, and when the proportions reach about  $20\text{FeCl}_3$  to  $1\text{KI}$ , the whole of the theoretically possible iodine is liberated, or, in other words, the reaction is complete.

In the second part of this paper the authors propose to discuss the theory of this reaction.

L. T. T.

**Atomic Weight of Palladium.** By E. H. KEISER and Miss M. B. BREED (*Amer. Chem. J.*, 16, 20–28).—The authors have prepared palladium diammonium chloride from palladium dichloride purified by distillation in a current of chlorine, and from metallic palladium, which was dissolved in *aqua regia*, the solution freed from acid by evaporation, treated with excess of ammonia, warmed, filtered, and the dichloride precipitated with gaseous hydrogen chloride. Both these methods give a product of undoubted purity, and one in which the ratio of palladium to palladium diammonium chloride is such as is equivalent to an atomic weight of 106.25 for palladium (mean of 10 determinations:  $\text{H}=1$ ;  $\text{N}=14.01$ ;  $\text{Cl}=35.37$ ), a number very closely agreeing with 106.27, that obtained by Keiser in previous determinations (compare *Abstr.*, 1890, 17). The method employed for converting the double salt into the metal was that of heating it in a current of pure hydrogen, and the experiments were conducted in such a way as to conclusively establish the fact that no loss of palladium occurred

by volatilisation or decrepitation (compare Keller and Smith, *Abstr.*, 1893, ii, 73).  
G. T. M.

## Mineralogical Chemistry.

**Artificial Trona.** By B. REINITZER (*Zeit. angew. Chem.*, 1893, 573—575).—The author notes an error in a reference to his work by C. Winkler (*Abstr.*, 1893, ii, 577), in that the analyses made by him in 1887 did not lead to the formula for trona then generally accepted, but to the formula  $\text{Na}_2\text{CO}_3 + \text{NaHCO}_3 + 2\text{H}_2\text{O}$ . This formula is identical with that given by Winkler.

In a subsequent communication, C. WINKLER (*Zeit. angew. Chem.*, 1893, 599) corrects the error, and explains how it originated.

B. H. B.

**Composition of Staurolite.** By S. L. PENFIELD and J. H. PRATI (*Amer. J. Sci.*, 47, 81—89).—In the early analyses of staurolite, especially in those by Rammelsberg, a great variation was found in the chemical composition, especially in the amounts of silica, which varied from 27 to 50 per cent. Formulæ proposed at different times show the following variations:— $\text{H}_4\text{Fe}_6\text{Al}_{24}\text{Si}_{12}\text{O}_{86}$  (Rammelsberg);  $\text{H}_4\text{Fe}_6\text{Al}_{24}\text{Si}_{11}\text{O}_{86}$  (Friedl);  $\text{H}_4\text{Fe}_6\text{Al}_{14}\text{Si}_{10}\text{O}_{82}$  (Coloranio). From a consideration of the analyses of Friedl and Coloranio, Groth suggests the simple formula of a basic orthosilicate  $(\text{AlO})_4(\text{AlOH})\text{Fe}(\text{SiO}_4)_2$ . That this formula is correct is well established by careful analyses made by the authors. These gave the following mean results:—

	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{FeO}$	$\text{H}_2\text{O}$	Sp. gr.
St. Gothard.. .. .	27.70	55.04	15.07	2.19	3.748
Windham, Maine .. .	27.60	55.75	14.43	2.20	3.728
Lisbon, New Hampshire .	27.44	55.16	15.72	1.68	3.775
Burnsville, N. Carolina..	27.47	55.83	14.74	1.96	3.773

From a comparison of the analyses with the results required by the formula, it will be observed that the silica is uniformly a trifle high. The authors are of opinion that quartz is an impurity in the mineral, and that it is present as very minute inclusions.  
B. H. B.

## Physiological Chemistry.

**Calorimetry.** By A. D. WALLER (*Proc. physiol. Soc.*, 1893, 25—29).—The ordinate of a thermographic curve may be taken as an index to the rate of heat discharge per area per time, and the area of a thermographic variation can be expressed in calories. For practical

comparisons, the area of such a variation may be taken as that of a triangle with time as base and maximum ordinate as height.

From this, the idea sprang that for clinical purposes an ordinary thermometer might be employed for calorimetry. A mercurial manometer with an excursion of 5 mm. per  $1^{\circ}$  indicated the increased heat discharge (for instance, that consequent on muscular exertion) far better than a partial calorimeter surrounding a limb. Loss of heat by evaporation is separately estimated.

The calorimetric value of surface thermographic or thermometric readings was estimated by experiments with an india-rubber sphere containing a known weight of cooling water, readings being taken at intervals from internal and external thermometers. A third thermometer gives the temperature of the air.

The rate of cooling is not strictly proportional to the temperature difference (T.D.), but more precisely to (T.D.)<sup>1.28</sup>; but the discrepancy is slight, and in any case easily corrected in a graduation scale.

The following numbers represent the state of heat emission from a human fore-arm with a superficial area of 500 cm<sup>2</sup>., after rest and after exertion. The surrounding temperature was  $20^{\circ}$ , and the evaporation gauged as described below.

	After rest.	After exertion.
T.D. ....	$12^{\circ}$	$14^{\circ}$
i.e. heat emission ..	75 cal. per minute	90
Moisture.....	4 mgrs. per 20 cm <sup>2</sup> . per minute	30
i.e. heat emission ..	6 cal. per minute	45
Total .....	81 cal. per minute	135

The water is estimated by means of shallow glass capsules, in the bottom of which calcium chloride solution had been evaporated to dryness. The capsule is weighed before and after it is inverted for a given time over an area of the surface of the body. With an external temperature of  $20^{\circ}$ , the following values (in milligrams, per 20 cm<sup>2</sup>. per 10 minutes) were observed. Palm of hand, 24; sole of foot, 12; forehead, 12; cheek, 6; axilla, 10; popliteal space, 10; forearm, 5; leg, 5.

W. D. H.

**Asphyxia.** By H. KRONECKER and JORDI (*Proc. physiol. Soc.*, 1893. 21—23).—The primary object of respiration is either to supply the organism with oxygen or to remove carbonic anhydride from it. A frog's heart will work as effectively when supplied with blood freed from its gases or with oxygenated blood; on the other hand, blood containing carbonic anhydride interferes with the heart's action, finally paralysing it. The heart beats again on removal of the carbonic anhydride (McGuire). Fishes can recover from asphyxia if opportunity be afforded to the blood of freeing itself from carbonic anhydride, by combination with substances introduced into the surrounding medium (Traube-Mengamio). Gold fish can live for two days and a half in a litre of water entirely shut off from air, and for about a day in boiled water. If, then, they are, in a dying condition,

conveyed to another litre of boiled out water, they recover, and survive 10—17 hours. Fresh fish introduced into the water tenanted by the dead fish live for some hours; but when a little sodium hydroxide is added they live a whole day. Fish die in water charged with carbonic anhydride, the amount of gas varying directly as the rapidity of death.

Further experiments, performed on the person of one of the authors, were designed to determine how much carbonic anhydride can be supported in inspired air. The gaseous mixture was inhaled from a gasometer of 40 litres' capacity. Equal parts of air and carbonic anhydride caused spasm of the glottis, and consequent inability to breathe at all. 30 per cent. of carbonic anhydride was breathed for a minute, the aspect of the subject of the experiment being dyspnoic; 22 per cent. of the gas caused less inconvenience; and a proportion of 8 per cent. caused much more ample breathing than normal. It was also found that an increase in the amount of carbonic anhydride produced in the body, as by the ascent of a tower, caused considerable stimulation of the respiratory efforts, and in one experiment voluntary maximum inspirations were continued for an hour.

W. D. H.

**Respiratory Exchange in Rabbits.** By M. S. PEMBERTON and A. GÜRBER (*J. Physiol.*, 15, 449—463).—The gases were analysed by Haldane's method. Rabbits were found to vary considerably in the amount of gases exchanged and in the respiratory quotient. The chief point investigated in the present paper is the influence of bleeding and transfusion on the gaseous interchange; and it was found that severe bleeding, even if half of the animal's blood is removed, whether followed by transfusion or not, causes no decrease in the respiratory exchange, provided the animal's nutrition does not suffer from the operation. If, however, the hæmoglobin is reduced to one-third of its normal value, the animal dies in convulsions. The experiments present another proof that vital combustion processes occur chiefly in the tissues of the body, not in the blood.

W. D. H.

**Gases in the Air-Bladder of Fishes.** By C. BOHR (*J. Physiol.*, 15, 494—500).—The gas in the air-bladder of fishes is a true secretion of a highly oxygenated gaseous mixture. The secretion appears to be under the control of the nervous system, and it fails when the branches of the vagus nerve which supply the air-bladder are cut.

W. D. H.

**Action of Digestive Ferments on Nuclein Compounds.** By P. M. PUPOFF (*Zeit. physiol. Chem.*, 18, 533—539).—A calf's thymus was divided into three parts. Part 1 was subjected to artificial gastric digestion for one hour. The undissolved residue contained 2.56 per cent. of phosphorus; the filtrate 0.243.

Part 2.—Here digestion went on for two hours. The percentage of phosphorus was then 2.66 in the residue.

Part 3.—Here digestion went on for three hours. The percentage of phosphorus in the residue was then 2.9.

A similar experiment with pancreatic fluid showed a much more rapid solution of the phosphorus-containing substance. So probably,

though but little nucleïn is digested in the stomach, a considerable quantity is absorbed after pancreatic digestion in the intestines.

W. D. H.

**Nucleïn in Nutrition.** By GUMMICH (*Zeit. physiol. Chem.*, 18, 508—512).—The nucleïn used was obtained from the thymus gland, and was given to dogs, the urine of which was examined. The effect was not marked, except in producing an increase in the phosphoric acid. There was no increase in the uric acid.

W. D. H.

**Nucleïn Bases in the Body.** By Y. INOKO (*Zeit. physiol. Chem.*, 18, 540—544).—The amounts of various bases derived from nucleïn were estimated in various organs (testis, pancreas), and in spermatozoa of various animals. It was found in all cases that xanthine bases are more abundant than sarkine bases, but the relation between them varies. Of the xanthine bases, those rich in oxygen (hypoxanthine and xanthine) are more abundant than those rich in nitrogen (adenine and guanine), the proportion varying from 2:1 to 3:2.

W. D. H.

**Hepatic Glycogenesis.** By D. NOËL PATON (*Proc. Roy. Soc.*, 54, 313—318).—Much recent research has tended to show that Bernard's original teaching concerning the glycogenic function of the liver is correct. The question whether the change of glycogen into sugar is due to a ferment action, or to the vital action of the liver cells is, however, undecided, and the object of the present paper is to elucidate this point. The question is considered how far the process is dependent on the life of the liver cell. The excised organ, roughly minced, was kept at 37—40° in normal salt solution, and it was found that during the first half hour the loss of glycogen was very rapid; after that it went on more slowly. In other experiments the liver substance was killed by grinding it with sand. These, compared with control specimens in which the liver was roughly minced, showed a much slower disappearance of glycogen. The histological changes occurring in the liver cells are also described. The conversion of glycogen into sugar is divisible into two periods: (1) an early period of rapid conversion occurring before obvious structural changes are seen in the cells; (2) a late period of slow conversion after these changes have developed. The rapid and extensive changes occurring in the first period is inhibited by destroying the cells, and is due to their vital activity; the second slower stage is believed to be due to the action of an enzyme.

The influence of various agencies in distinguishing between the two processes is next described; namely, of a temperature of 60°, which inhibits vital but not the fermentative activity—and of sodium fluoride (1 per cent. solution), which acts similarly.

Chloroform was found to increase hepatic amylolysis markedly; and it is the early rapid amylolysis which is accelerated, the microscope revealing a more rapid katabolic change in the cells than the normal. Some experiments performed during life show that chloroform anæsthesia then increases hepatic amylolysis also.

Ether acts like chloroform but in a smaller degree. Pyrogallio acid

(0.25 per cent. solution) acts in the same way. Morphine, curare, amyl nitrite, and sodium salicylate have no action.

The development, after death, of an acid reaction, due in part to lactic acid, is not the cause of amyolysis. The influence of micro-organisms is also excluded.

In the first rapid amyolysis, glucose is formed; intermediate substances of the nature of dextrins and maltose were not detected. In the later amyolysis, dextrins (and possibly maltose) were always found. W. D. H.

**Chemistry of Muscle.** By H. BORCHARD (*Zeit. physiol. Chem.*, 18, 513—524).—The glycogen of heart muscle diminishes after death more rapidly than that of skeletal muscles under the same conditions. Heart muscle or its aqueous extract changes glycogen into sugar more rapidly than skeletal muscle or its aqueous extract. The original percentage of glycogen in the fresh heart muscle is about the same as in skeletal muscle.

Inosite is more abundant in heart muscle than in skeletal muscle. Heart muscle is neutral in reaction; when tetanised, or after death, it turns acid. W. D. H.

**Elastic Substance of the Aorta.** By H. SCHWARZ (*Zeit. physiol. Chem.*, 18, 457—507).—Elastin was obtained from the aorta by taking advantage of its relative indigestibility in artificial gastric juice. It is identical with that obtained from the *Ligamentum nuchæ*. Elastin contains sulphur, which is removable by boiling with 1 per cent. potassium hydroxide; this, however, does not destroy the elastin, which still retains its characteristic properties. With superheated steam, it yields hemi-elastin and elastin-peptone (proto- and deuterio-elastose). Decomposed by hydrochloric acid, it yields ammonia, hydrogen sulphide, leucine, glycocine, tyrosine, homologous benzoic acids, and lysatinin. By fusion with alkali, it yields, among other products, indole, skatole, benzene, and phenol. W. D. H.

**Chemistry of Leucocytes.** By L. LILIENTHAL (*Zeit. physiol. Chem.*, 18, 473—486).—The leucocytes were obtained from the thymus gland by the use of pressure and the centrifuge. The aqueous extract contained a proteid coagulating at 48° and another coagulating at 73—75°. A nucleo-albumin was also obtained by Halliburton's method; it was found to contain C, 53.46; H, 7.64; N, 15.57; and P, 0.433 per cent. The alcoholic extract of the cells contained protagon, amidovaleric acid, inosite, and mono-potassium phosphate.

A nuclein-containing proteid, called nucleo-histon, was obtained by precipitating with acetic acid an aqueous extract of the cells. [This is what Wooldridge termed "tissue-fibrinogen."—Abstractor.] Its elementary composition is C, 48.46; H, 7.0; N, 16.86; P, 3.025; S, 0.701 per cent. The action of artificial gastric juice, or of 0.8 per cent. hydrochloric acid, on this is to separate the nuclein from the proteid, which goes into solution as peptone. The nuclein contains

4.991 per cent. of phosphorus. Nucleic acid prepared from this contains 9.94 per cent. of phosphorus.

Histon, the other constituent of nucleo-histon, was first obtained from birds' red corpuscles by Kossel (*Zeit. physiol. Chem.*, 1884), who described it as a peptone-like substance; many have since regarded it as an artificial product, formed by the acid used in its preparation. This view is combated in the present paper. Leucohiston, however, differs from Kossel's compound in being coagulable by heat.

The following table gives the quantitative composition of leucocytes.

Water .....	88.51
Solids .....	11.49

100 parts of the solids contain—

Total phosphorus .....	3.01
Total nitrogen.....	15.03
Proteid .....	1.76
Leuconuclein.. .....	68.78
Histon .....	8.67
Lecithin .....	7.51
Fat .....	4.02
Cholesterol.....	4.40
Glycogen .....	0.80

The weight of the silver compounds of the nucleic bases (adenine, hypoxanthine) obtained was 15.17. W. D. H.

**Fluorine in Bones and Teeth.** By S. GABRIEL (*Zeit. anal. Chem.*, 33, 53—54).—To the conclusion arrived at by Gabriel (*Abstr.*, 1893, ii, 82), that teeth contain only traces of fluorine, Wrampelmeyer has objected, on the ground that organic substances cannot be incinerated without loss of fluorides. The author replies that it is impossible to assume the loss of 1 per cent. of fluorine; that the results obtained by Brandl and Tappeiner (*Abstr.*, 1893, ii, 23) tend to negative any important loss on incineration; that his own results do not depend entirely on the examination of the ash of teeth, but also on the extraction of the powdered bone with alkaline glycerol; and, lastly, that his communication, above quoted, was only a preliminary one, the whole subject being exhaustively treated later, (*this vol.*, ii, 21). M. J. S.

**Composition of the Liver Fat of "Birgus latro."** By E. GÉRARD (*J. Pharm.*, [5], 28, 443—450).—The purified fat obtained from this crab melts at 24°, and gives, by saponification, glycerol and a mixture of fatty acids melting at 26° to 27°. Of these, the acids which form barium salts soluble in hot water, are lauric, caproic, and caprylic. The other acids are stearic and palmitic. The mixture contains cholesterol, but no unsaturated acids. W. T.

**Colour of Lepidopterous Larvæ.** By E. B. POULTON (*Proc. Roy. Soc.*, 54, 417—430).—Previous researches having shown that



probably certain elements of the colouring of butterflies' larvæ are modified chlorophyll (metachlorophyll), derived from the food plant, a critical experiment is now described. The larvæ of *Tryphæna promuba* were arranged in three sets, fed respectively on (1) the yellow, etiolated leaves from the heart of the cabbage; (2) the white mid-ribs of such leaves, from which the yellow blades were carefully removed: and (3) the deep green external leaves. Those in the first and third sets became green or brown, those in the second set remained colourless, but the greater number died during the experiment.

W. D. H.

**Nature and Causes of the Green Colour of Oysters.** By A. CHATIN and A. MUNTZ (*Compt. rend.*, 118, 17—23 and 56—58).—Oysters, as Berthelot stated some years ago, do not contain chlorophyll, but they contain iron, which is concentrated chiefly in the gills, where the green colour is deepest, and amounts to from 0.06 to 0.08 per cent. of the dry matter. In the rest of the oyster, it amounts to from 0.025 to 0.048 per cent. It is noteworthy that in brown oysters the percentage of iron is practically the same, and it is likewise concentrated in the gills, where the brown colour is deepest. The mud at the bottom of the cultivating tanks contains in 1000 parts: N, 0.79 to 1.92;  $P_2O_5$ , 0.75 to 2.10;  $SO_3$ , 6.33 to 34.18; Cl, 8.44 to 23.71; I, 0.0005 to 0.005; CaO, 5.60 to 110.60;  $Fe_2O_3$ , 17.04 to 77.79. In two cases, the nitrogen is as high as 6.22 and 7.55, respectively; in one, the phosphoric anhydride is as low as 0.15, and in another, 0.43; in two cases, the calcium oxide is 219.8 and 213.36 respectively. The muds contain a considerable quantity of iron in the form of ferrous oxide and ferrous sulphide. When the mud is exposed to air during the summer months, in accordance with the usual practice, its black colour gradually changes to brown, the ferrous sulphide and oxide being oxidised, and the ammoniacal nitrogen converted into nitrates. Part of this oxidation is due to the action of algæ, which develop rapidly under the influence of light, and decompose the carbonic acid in the water, liberating nascent oxygen in contact with the ferrous compound.

C. H. B.,

**Potassium Thiocyanate in the Stomach.** By G. KELLING (*Zeit. physiol. Chem.*, 18, 397—406).—It is shown that potassium thiocyanate is present in the stomach contents; it may be recognised by the ferric chloride reaction, and presumably comes from the swallowed saliva. The amount of hydrochloric acid in the stomach makes a difference in the reaction. If saliva is mixed with dilute hydrochloric acid, carbonic anhydride comes off, and the ferric chloride reaction is weaker. On the addition of stronger hydrochloric acid, the intensity of the reaction increases in time.

The presence of potassium thiocyanate is a source of error in Uffelmann's reaction for lactic acid.

W. D. H.

**Secretion of Myxine Glutinosa.** By E. W. REID (*J. Physiol.*, 15, 488—493).—The slime of this fish contains two substances, a granule substance and a thread substance (*Abstr.*, 1893, ii, 429); the

former was dissolved in 0.01 per cent. solution of potassium hydroxide, leaving the threads unaffected; the granule substance was precipitated from solution, either by 1 per cent. solution of acetic, or 0.1 per cent. of hydrochloric, acid.

The granule substance resembles mucin in many of its characters; it, however, yields no reducing substance on treatment with sulphuric acid. It, moreover, contains phosphorus, although it is completely soluble in artificial gastric juice.

The thread substance appears to be a more insoluble variety of the same material. It is insoluble in gastric juice, but is stated to contain less phosphorus than the granule substance; accurate quantitative experiments are, however, not given.

W. D. H.

**Excretion of Nitrogen in Diabetes.** By H. LEO (*Chem. Centr.*, 1893, ii, 603; from *Zeit. klin. Med.*, 22, 223—224).—In normal individuals, a test meal containing 75 grams of cane sugar, 50 grams of butter, and 120 grams of maize, causes a marked rise in the excretion of nitrogen. In diabetics, the same occurs, the rise in nitrogenous output running almost parallel with that of the volume of urine and amount of sugar therein. Shortly afterwards a fall occurs. The rise of nitrogen is, as a rule, more marked than in normal persons. In one case, an increase in the carbohydrates of the food led to a diminution in the urinary nitrogen; and, although the proteid-sparing action of carbohydrates is not always seen in diabetes, it is the general rule.

W. D. H.

**Passage of Chloroform, administered by Inhalation, into the Urine.** By P. VITALI (*L'Orosi*, 16, 299—304).—Bréaudat (*J. Pharm. Chim.*, 1893, 194) was unable to find chloroform in the urine after its administration as an anæsthetic; the author, however, employing the very sensitive process given below, in some cases found traces of chloroform in the urine. A current of pure hydrogen is passed through the urine, or any other liquid containing chloroform; the latter is thus carried off as vapour, and on burning the hydrogen and allowing the flame to play on a piece of fine brass gauze, the wire assumes a bluish-white colour. On drawing off the products of combustion from the gauze, and passing them through ammonia solution, a bluish coloration is obtained, and the solution is found to contain chlorine. The quantity of chloroform found in the urine after inhalation of the anæsthetic is always very small, and in some cases none can be detected.

After administration of chloroform, the urine always reduces the solutions of Fehling, Trommer, and Böttger, and gives a white turbidity when boiled with mercuric chloride solution; this is not due to the presence of glucose. This result is in agreement with those obtained by Kast, v. Mering, and Zeller, but opposed to those of Bréaudat. The author also shows that, after inhalation of chloroform, the urine contains organic chlorine, although it does not seem to be present as trichloromethylglycuronic acid, or its homologue.

W. J. P.

**South American Meat Extract and Meat Peptone.** By E. KEMNERICH (*Zeit. physiol. Chem.*, 18, 409—422).—The methods of analysing these preparations of the author are described.

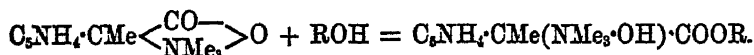
The extract contains 15—18 per cent. of water, 6.19 of gelatin, 14.16 of albumoses, 12.31 of peptone, a total proteid percentage of 33.23. There is also present 20 to 22.3 per cent. of mineral matters (chiefly phosphates), 1.22 of glycogen, 4.33 of creatinine, 0.25 to 1 of carmine, 1 of fat, 0.9 of ammonia, and 18 to 22 of other extractives.

The meat peptone contains more proteid, 18.75 of soluble albumin and gelatin, 39.16 of albumose and peptone; a total of 57.91.

The glycogen is present in well-preserved specimens made from fresh meat.

The presence of creatinine—not creatine—confirms G. S. Johnson's work (*Proc. Roy. Soc.*, 50, 28). W. D. H.

**Physiological Action of Pilocarpine.** By A. CURCI (*Chem. Centr.*, 1893, ii, 659; from *Annali Chim. Farm.*, 18, 3—8).—Pilocarpine produces hyper-secretion, convulsions, and paralysis. The paralysis is accounted for by regarding pilocarpine as a quaternary ammonium compound. But phenol and oximhydroxyl groups, the most powerful in producing hyper-secretion and convulsions, are absent. It is not improbable, however, that in the organism changes may occur, a pilocarpinate being formed with the bases of the body; thus:—



In dogs, the drug leaves the body in the urine partly as free pilocarpine and partly as such a pilocarpinate. W. D. H.

**Crystalline Substance in Silkworms destroyed by Muscardine.** By E. VERNON (*Staz. Sper. Agrar.*, 24, 245—255).—The disease known as "Muscardine," and caused by *Botrite Bassiana*, gives rise to a crystalline efflorescence on the dead silkworms. This efflorescence was examined by Brugnatelli, at the instance of Dandolo. In a note by Dandolo (1814), the substance is stated to consist chiefly of magnesia, phosphoric acid, and ammonia. After describing the appearance of the substance under different atmospheric conditions, the author gives in detail his method of purification and analysis. The following results were obtained: water lost at 100°, 12.635; oxalic acid, 48.975; ammonia, 22.365, and magnesia, 1.9 per cent. These numbers point to the formula,  $C_2O_4.Mg.5C_2O_4.(NH_4)_2 + 10H_2O$ . The action of *Botrite Bassiana* is probably limited to the production of oxalic acid, a small portion of which is neutralised by magnesia, whilst most of it combines with the ammonia liberated in the decomposition of the silkworm. N. H. M.

## Chemistry of Vegetable Physiology and Agriculture.

**Action of Calcium Sulphite and of Hydrogen Potassium Sulphite on Alcoholic Fermentation.** By F. RAVIZZA (*S'az. Sper. Agrar.*, 24, 593—609).—The want of agreement of the results obtained by Czeppel (*Bull. Soc. Viticoll.*, 1880, 625, and 1892, 47) and those of Chiaromonte (this vol., ii, 61) is shortly discussed. In the first experiments, now described, must (sp. gr. 1·0765), containing a solution of invert sugar and an excess of tartaric acid, was treated with varying amounts of calcium sulphite (0·05 to 0·5 per litre), the temperature and amounts of carbonic anhydride evolved being observed daily. Under the conditions of the experiments, with a temperature of 30°, the sulphite had no effect, either in lowering the temperature or in increasing the activity of the ferment. The next experiments were similar to the first, but hydrogen potassium sulphite was employed instead of the calcium salt, and the temperature was much lower (14°). With 0·05 and 0·15 gram of sulphite there was less evolution of carbonic anhydride for the first two weeks than when no sulphite was added; but after that the amounts were much the same. With larger amounts of sulphite, the fermentation was stopped. A third series of experiments was made in which the effect of calcium sulphite was directly compared with that of hydrogen potassium sulphite, both at 35° and at 15°. At the higher temperature, 1·2 gram of calcium sulphite per litre and 0·3 gram of the potassium salt were practically without effect; 0·5 gram of hydrogen potassium sulphite stopped the fermentation. At 15°, the amounts of calcium salt employed were almost without effect after a few days; 0·30 gram of the potassium salt retarded the fermentation somewhat, even to the end, whilst 0·5 gram, as at 35°, stopped it altogether.

Experiments were made to ascertain the effect of the two salts on *saccharomyces*, by determining the number of colonies from 1 c.c. of wine at different dates after treatment with 0·01 gram per litre of each salt. Without any addition the number of colonies increased in 15 days to about 20 times the original number; with the calcium salt, the number was reduced to about a seventh, whilst with hydrogen potassium sulphite the number was reduced to almost nothing (one-seventieth).

The results of the author's experiments are opposed to those obtained by Czeppel (*loc. cit.*), and resemble Chiaromonte's. As regards hydrogen potassium sulphite, it is much more active than calcium sulphite, and, when further studied, will be probably substituted for it in the treatment of wines, whether to subdue the fermentation, or to give wine a greater power of resisting hot summers, or for sending wines to distant countries. Before recommending its use, however, more experiments should be made with natural musts. N. H. M.

**Formation of Carbonic Anhydride and Absorption of Oxygen by Leaves after their Removal from Plants.** By BERTHELOT and G. ANDRÉ (*Compt. rend.*, 118, 45—54 and 104—112).—When

leaves of wheat, hazel (*Corylus avelana*), and *Sedum maximum* are heated at 100–110° in a current of hydrogen, carbonic anhydride is evolved in quantity amounting to about 0.7 per cent. of the dry matter. The evolution of gas takes place in two stages, namely, at 94–99°, and at 110° after desiccation is practically complete. In a current of air instead of hydrogen, the phenomena are similar, carbonic anhydride being evolved in two stages corresponding respectively with the evolution of the greater part of the water, while the temperature inside the flask is about 100°, and with the period when leaves have become practically dry, and the temperature of the flask has risen to about 110°. The quantity of carbonic anhydride evolved is greater than in a current of hydrogen.

If similar leaves are immersed in water and heated at 100° in a slow current of air, the quantity of carbonic anhydride evolved in the case of wheat is greater than in the previous experiments with a current of hydrogen, but less than with a current of air. It would seem that the oxygen under the conditions specified is only able to act on the leaves after it has dissolved in the water. With hazel leaves, the results are similar to those obtained in hydrogen, and with leaves of *Sedum maximum* the quantity of carbonic anhydride given off is greater than in the previous experiments with either air or hydrogen.

The moist leaves were heated at 100°, in a closed vessel filled with oxygen, and the amounts of carbonic anhydride formed and oxygen absorbed were determined. It was found that the volume ratio,  $O_2/CO_2$ , was 1.32 for wheat, 1.60 for hazel, and 1.90 for *S. maximum*. The quantity of carbonic anhydride formed is in all three cases much greater than in hydrogen. The quantity of oxygen absorbed without production of carbonic anhydride is greatest in the case of hazel leaves, and least with the leaves of *S. maximum*, and it is noteworthy that the former contain the lowest and the latter the highest proportion of water.

When these leaves are allowed to dry gradually at the ordinary temperature, the quantity of carbonic anhydride given off is much greater than at 100–110°. The leaves of *S. maximum* dry very slowly, and the phenomena are complicated by the development of *mucidinae* towards the close of the operation. The increased evolution of carbonic anhydride during drying is due to biological processes. Some carbon is evolved in the form of volatile compounds, the nature of which has not yet been determined. The nitrogen and the ash, however, remain unchanged in amount throughout the process. The hydrogen is eliminated, either in the form of water or of other compounds in which the ratio of hydrogen to oxygen is the same. Practically, the whole of the oxygen in the carbonic anhydride evolved is derived from the air, and not from the leaves, and hence the formation of carbonic anhydride is not due to the action of anaerobic ferments. The volume ratio of carbonic anhydride evolved to oxygen absorbed is practically unity, as in the respiration of animals.

When moist leaves are placed in a vessel filled with oxygen at the ordinary temperature, so that the leaves do not become dry, carbonic anhydride is evolved, and oxygen is absorbed, and at first these

changes seem to be due chiefly to the internal reactions of the leaves, but, after a time, moulds develop, and produce special effects of decomposition and slow combination. During the first week, the volume ratio,  $O_2/CO_2$ , is practically unity, but afterwards oxygen is absorbed in excess of that corresponding with the carbonic anhydride. With hazel leaves, if the action of the oxygen is prolonged, the weight of carbonic anhydride formed may rise as high as 41 per cent. of the weight of the substance, whilst the weight of oxygen absorbed is as high as 70.3 per cent. Neither alcohol nor acetic acid is formed. The nitrogen remains unchanged in amount.

In all cases, it would seem that the phenomena are due to the breaking up of several of the primary glucogenic molecules, which are the generators of the carbohydrates present in the leaves, the carbon being converted into carbonic anhydride, and the hydrogen into water, just as in the nutrition of animals. The quantity of heat developed by these changes is about one-fourth of the heat developed in the animal organism, as measured by the rise of temperature that it is capable of producing in the body undergoing oxidation.

C. H. B.

**Method of Investigating the Exchanges of Gases between Living Organisms and the Surrounding Atmosphere.** By BERTHELOT (*Compt. rend.*, 118, 112—114).—The animal or plant is enclosed in a vessel so large that the normal course of respiration, &c., is not interfered with, and from time to time known volumes of gas are expelled by introducing known volumes of air, and the expelled gas is analysed. In the case of the action of air on leaves, for instance, the carbonic anhydride is absorbed by potassium hydroxide.

If the capacity of the vessel is  $V$ , and the total weight of the gas to be estimated is at a particular time,  $p$ , then, if a very small bubble of air is introduced,  $v$ , and is allowed to diffuse uniformly through the vessel (that is, the current of air must be very slow), a volume of gas,  $v$ , will be expelled from the vessel. This volume will contain a weight of the gas to be estimated,  $p \frac{v}{V}$ , and there will remain in the vessel  $p \left(1 - \frac{v}{V}\right)$ . After  $n$  bubbles the quantity remaining will be  $p \left(1 - \frac{v}{V}\right)^n$ . Assuming that  $nr = V$ , and  $v$  being very small, it follows that

$$p\left(\frac{1}{2} - \frac{1}{6} + \frac{1}{24} - \frac{1}{120} \dots\right) = 0.368 \dots p,$$

and after  $m$  similar operations  $p (0.368)^m$  practically. Divergences from these ratios indicate that some absorption or evolution of gas is taking place; and it is clear that since the removal of the gas for analysis in no way interferes with the course of the experiment, the investigation may be carried on continuously.

C. H. B.

**Nitrates in Living Plants.** By DEMOUSSY (*Compt. rend.*, 118, 79—82).—Berthelot and André showed that nitrates are always present in plants, and pointed out their importance to vegetation

(compare also Dehérain, this vol., ii. p. 156). The power of retention of nitrates by living plants, and the absence of such power in the case of dead plants, is shown by the following experiment:—Some meadow-grass, including tops and roots, was divided into three lots of 100 grams (22 grams of dry matter). The first sample was kept for 24 hours in cold water. At the end of this time, the plant was distinctly coloured by diphenylamine sulphate, whilst the water only contained 0.1 milligram of nitrogen. On extracting the substance with boiling water, 21.9 milligram of nitric nitrogen was obtained. The second sample was dried and then extracted with hot water; 22.6 milligrams of nitric nitrogen was obtained, whilst the root no longer gave any reaction with diphenylamine sulphate. The third portion was subjected for an hour to the action of chloroform vapour, and then kept for 24 hours in cold water (1 litre). The root gave only a very slight reaction with diphenylamine, and none at all after being washed a little. The extract contained 21.3 milligrams of nitric nitrogen.

Notwithstanding their solubility, nitrates are held by the protoplasm with an energy comparable with chemical affinity. Dead leaves and roots become easily deprived of nitrates by rain; but Berthelot frequently found considerable amounts of nitric acid in above ground portions of plants which died during a period of dry weather.

N. H. M.

**Copper in Various Parts of the Vine.** By F. SESTINI (*Staz. Sper. Agrar.*, 24, 115—132).—The first plants examined had been watered with a solution of copper sulphate. The plants grew well in the spring, but became sickly in the summer, and died in the autumn. This was possibly due to injury by the large amount of mineral manures, phosphates, sodium nitrate, &c., applied; but probably their destruction was largely due to the copper salt. The air-dried roots contained (1) 0.0547 and (2) 0.1307 per cent. of copper, whilst a portion of the stem (without leaves) contained only 0.0013 per cent. Four samples of leaves of plants which had not been treated with copper salts contained respectively 0.00047, 0.00056, 0.00060, and 0.00054 per cent. of copper. New shoots of vines, which had been treated with copper about three months previously, contained 0.00073 per cent. of copper; the leaves contained 0.00063, and the tendrils 0.00011 per cent. New shoots from other plants contained 0.00053 per cent., whilst the older leaves contained 0.00118 per cent. of copper.

Most of the copper found in vines will be in those portions to which it was directly applied, as there is very little circulation within the plant; consequently, those portions which are not directly treated with copper salts will contain only about the quantity usually found in vines to which no copper has been applied. N. H. M.

**Cane Sugar in Seeds of Plants, Raffinose in Wheat Germs, Crystalline Lævulin.** By E. SCHLZE and S. FRANKFURT (*Ber.*, 27, 62—64, 64—65, and 65—66).—The cane sugar is obtained from the alcoholic extract of the seed, by precipitation as the strontia compound, and the precipitate is then decomposed by carbonic anhydride,

and treated according to the method already described by the authors (*Landw. Versuchs-Stat.*, 34, 415).

By this method the authors have obtained cane sugar from the seeds of *Triticum vulgare*, *Secale cereale*, *Avena sativa*, *Polygonum fagopyrum*, *Cannabis sativa*, *Helianthus annuus*, *Pisum sativum*, *Soja hispida*, and *Coffea arabica*.

Cane sugar has also been obtained from the seeds of *Vicia faba*, *Phaseolus vulgaris*, *Hordeum distichum*, *Zea mays*, *Arachis hypogaea*, *Corylus avellana*, *Juglans regia*, and *Amygdalus communis*; so that it is very widely distributed in seeds. The only seeds which gave a negative result were those of *Lupinus luteus*.

The authors confirm the result of Richardson and Crompton, who found cane sugar in wheat germ, (*Ber.*, 19, 1180).

Cane sugar was also obtained from the green shoots of the pea.

Raffinose is obtained from wheat germs by evaporating the sugar solution obtained by the above method to a syrup, and extracting the cane sugar with the requisite quantity of boiling alcohol. When the syrupy residue is mixed with absolute alcohol, a precipitate of raffinose is obtained. The product, after purification by recrystallisation, gave for a 10 per cent. aqueous solution  $[\alpha]_D = +105.5$ ; and, on oxidation with nitric acid, 22.2 per cent. of saccharic acid.

A carbohydrate which has all the properties of lævulin is obtained, together with cane sugar, from the stalks of rye gathered before the formation of seed commences. It is isolated in the same way as raffinose, from wheat germs. It crystallises in small prisms, and when dried over sulphuric acid forms a white powder, which quickly takes up water from the air; on analysis, it gave numbers corresponding with the formula  $C_{12}H_{22}O_{11}$ . It reduces Fehling's solution only after heating with an acid, and is optically inactive in aqueous solution.

E. C. R.

**Lecithin in Vegetable Substances.** By E. SCHULZE and S. FRANKFURT (*Landw. Versuchs-Stat.*, 1893, 307—325).—To obtain lecithin from seeds, they should be finely ground, treated with ether, and extracted with 50—60 per cent. alcohol, the alcohol evaporated, and the residue treated with ether; water should now be added to saturation, and the emulsion which is thus formed must be cleared by the addition of salt; after separation, the ether is evaporated, and the lecithin which is left, is purified by redissolving it in alcohol. To work quantitatively, the phosphoric acid must be determined in the alcoholic extract, and the lecithin calculated therefrom (factor: magnesium pyrophosphate  $\times 7.2703$ ). Full details are given, as also the percentage of lecithin in many seeds.

E. W. P.

**Sunflower Cake.** By T. KOSULANY (*Landw. Versuchs-Stat.*, 1893, 253—263). Sunflowers (*Helianthus annuus*) are largely grown in Hungary. The oil is expressed from their seeds, and the cake thus obtained is used as fodder for cattle. A vast number of seeds from all parts of the world have been analysed, and the constituents are found to vary considerably. Taking one sample only out of the many: the dried seed gave nitrogenous matter, 15.98; fat, 36.6; non-



nitrogenous extract, 19.39; fibre, 24.3; ash, 3.13 per cent.—air-dried seed (husked): water, 14.7; nitrogenous substance, 24.95; fat, 49.62; non-nitrogenous extract, 4.18; fibre, 3.28; ash, 3.27 per cent. The methods of preparing the cake and expressing the oil are described. E. W. P.

**Pumpkin-seed Cake.** By T. KOSUTANY (*Landw. Versuchs-Stat.*, 1893, 264—269).—Several analyses of the whole fruit of plants of different varieties of pumpkins are given. The dried seeds contain 41.1—53.96 per cent. of oil; the oil is largely used as food, and for burning. E. W. P.

**Composition of Winter Drainage from bare Soil and Soil sown with Wheat.** By P. P. DEHÉRAIN (*Compt. rend.*, 117, 1041—1045; compare Abstr., 1893, ii. 338 and 486).—In a previous paper, the amounts of nitric nitrogen collected early in 1892 from the Grignon vegetation cases were given; the present paper gives the results obtained with drainage from November, 1892, to March, 1893. The summer drainage from fallow soil contained 145 parts of nitric nitrogen per million, whilst in the four winter months it only contained an average of 92 per million—in December 183 and 157, in January 11 and 9, in February 78, and in March 116 per million. When the loss of nitrogen is calculated per hectare, it is found to be very great, being 81.185 kilos. in winter and 221.8 kilos. for the whole year, or nearly five times as much as the loss of nitrogen observed at Rothamsted (47 kilos. per hectare). This great difference is due to the titration of the Grignon soil, and the aeration which it underwent when put into the cases. A considerable diminution in the amounts of nitrates formed has already been observed. Thus, the drainage of December, 1893, contained only 93 parts of nitric nitrogen per million.

With regard to the loss from bare soil, as compared with soil covered with vegetation, a second case sown with rye-grass only lost 10.3 kilos. of nitrogen per hectare, as against 81.185 kilos. lost by fallow land; and the drainage contained only 13 parts of nitric nitrogen per million. Inasmuch as there was no reason to suppose that there was any essential difference in the nitrification of the two cases, it seemed likely that the nitric acid was retained by the plants. An examination of gramineous plants grown in the garden of the museum and in a Grignon meadow showed that the dry roots contained 0.062 and 0.375 per cent. of nitric nitrogen respectively, whilst the stems contained 0.113 and 0.039 per cent. These plants have, therefore, the power of storing up nitrates during the winter months for future use.

The richness of grass land in nitrogen, and the increase in richness observed at Grignon (from 1.5 per cent. in 1879 to 1.88 in 1888), is due partly to the nitrogen-fixing organisms (Berthelot), to cryptogamic vegetation (Schlossing, jun., and Laurent), and partly to the abstraction of nitrates from the water percolating through it.

Not only the ordinary grasses, but also wheat has the power of retaining nitrates in the winter; thus roots taken from the field in December contained 0.563 per cent. of nitric nitrogen (in the dry matter), whilst roots and stems taken from a bank next the field

contained respectively 1.041 and 0.187 per cent. The roots were at this time over 30 cm. long.

From March, 1892, to March, 1893, the four cases with bare soil lost 221.4, 193.1, 242.1, and 245.2 kilos. of nitrogen per hectare. Grass land lost in the same time only 30 kilos., and soils bearing successively beet and winter wheat lost 19.4, 17.6, and 40.6 kilos. per hectare. These comparatively slight losses are due to the much lessened drainage, and, as shown above, to the retentive power of the plants.

N. H. M.

**Influence of Iron on Barley.** By P. PETIT (*Compt. rend.*, 117, 1105—1107).—Barley was grown in sand freed from iron, to which the necessary ash constituents were added. There were four series of pots:—No. 1 had 0.00604 milligram of iron in the form of barley nuclein (4 grams; see Abstr. 1893, i, 539); No. 2 had 0.98 gram of iron as ferrous sulphate (5 grams); No. 3 had 0.999 gram of iron as ferric sulphate (4.4 grams); No. 4 had no iron at all. Nuclein and ferrous sulphate were both beneficial, whilst ferric sulphate acted as a poison. The following amounts of produce, dried at 50°, were obtained in each of the four series.

	I.	II.	III.	IV.
Stems .....	3.55	3.72	0.80	2.77
Leaves .....	5.29	3.88	0.81	3.95
Total produce for 1 gram of seeds..	48	40	9	39

The greatest increase was produced under the influence of the nuclein.

The dry matter of the stems and leaves contained the following percentage amounts of nitrogen, ash, and iron.

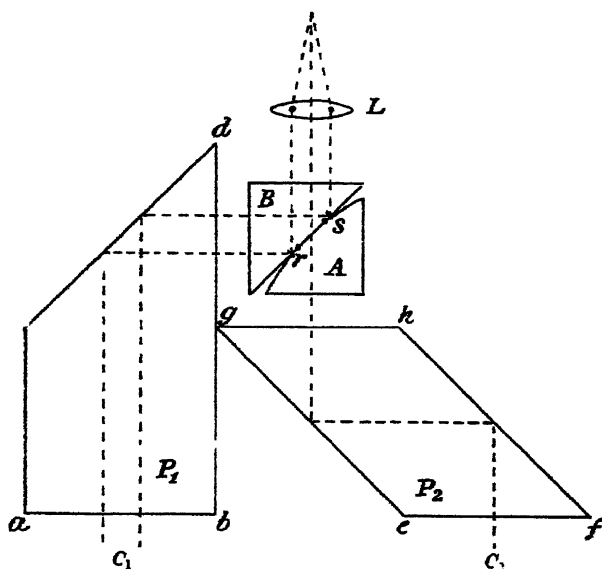
	Stems.			Leaves.		
	N.	Ash.	Fe.	N.	Ash.	Fe.
I .....	1.44	20.5	0.24	2.24	20.1	0.25
II .....	1.49	19.5	0.51	2.01	19.8	0.57
III .....	1.48	19.2	0.48	2.2	17.9	0.56
IV .....	1.31	20.5	0.05	1.81	16.9	0.05

As regards the stems, the amount of nitrogen was slightly increased by the nuclein and iron salts, whilst the iron was very greatly increased. In the leaves, the nuclein had a very marked effect on the nitrogen percentage.

N. H. M.

## Analytical Chemistry.

**Colorimeter with Lummer-Brodhun Double Prism.** By H. K $\ddot{u}$ ss (*Zeit. anorg. Chem.*, 5, 325—329).—In colorimeters it is, of course, of the greatest importance that the two fields to be compared should be as close together as possible. This is generally effected by means of two reflection prisms cemented together below the eye-piece. By this means the two fields are made to form the two halves of the field of vision. However closely the prisms are cemented together the line of contact is not a mathematical line, and, being magnified by the eyepiece, forms a dark line across the field of vision, thus preventing the formation of an unbroken field, and reducing the delicacy of the apparatus. The author has overcome this difficulty by the introduction of a Lummer-Brodhun double prism. This double prism consists of one ordinary total reflecting prism, with a perfectly plane hypothenuse surface, and one with the hypothenuse surface spherical, with only a small (circular) plane surface in the centre. This second prism is adjusted to the first, so that its plane circle is in the centre of the plane hypothenuse side of the other, and the two are pressed together so tightly that no air remains between the two plane surfaces in contact. In this way, a double prism is obtained in which light rays striking the contact surfaces pass through without change, whilst those striking the remaining portion of the plane hypothenuse surface are totally reflected. The arrangement of prisms, and the construction of the Lummer-Brodhun double prism will be readily seen from the annexed sketch. In this, AB is the Lummer-Brodhun



double prism, L the lens of the eyepiece, and the dotted line- C<sup>1</sup> and C<sup>2</sup> the path of the light rays from the two colour surfaces to be compared. By this arrangement C<sup>2</sup> is seen as a circle in the centre of the field of vision, C<sup>1</sup> as an annular space surrounding that centre. When the two colours are exactly equalised, there is no visible line of demarcation between the two surfaces, and greater accuracy is obtainable than heretofore. The combination of prisms is so arranged that each light ray has to pass through an equal distance of glass and be reflected an equal number of times, so that the two fields are maintained of equal brightness.

L. T. T.

**Estimation of Bromine in Urine.** By A. NICOLLE (*J. Pharm.*, [5], 28, 298—299).—The residue from the evaporation of 50 c.c. of urine to which has been added 2 grams of potash is heated to dull redness. The aqueous extract is made up to 40 c.c., and distilled with 20 grams of potassium dichromate and 10 c.c. of sulphuric acid, the distillate being collected in a bulb-tube containing 20–25 c.c. of a 4 per cent. solution of potassium iodide. The distillation is continued for about 15 minutes after the apparent conclusion of the evolution of bromine. The liberated iodine is titrated in the usual manner with sodium thiosulphate. If sulphur is present, the urine is boiled with barium chloride and hydrochloric acid, and filtered before evaporation; or, better, the aqueous extract, after incineration, is boiled with oxalic acid so long as hydrogen sulphide is evolved. If the urine contains iodides, the aqueous extract is neutralised and the iodine expelled by boiling with potassium dichromate, the sulphuric acid is then added and the distillation continued as usual.

W. T.

[*Note by Abstractor.*—Iodine is not completely expelled by boiling with the proportions of dichromate and solution given above. Chlorine is liberated at the same time as the bromine, to the extent of more than 3 per cent. of the quantity present.]

**Microchemical Examination for Iodine.** By G. DENIGÈS (*J. Pharm.*, [5], 28, 499—500).—The iodoform reaction is used and the precipitate examined microscopically for the characteristic hexagonal plates of iodoform. To apply the test, a solution is prepared containing the iodine as sodium or potassium salt. If in the form of iodate, it is reduced by the addition of a drop of sodium hydrogen sulphite solution. If the solution is very dilute, about 10 c.c. is taken, a drop of soda solution added, and then five or six drops of a 10 per cent. solution of acetone; finally, a solution of an alkali hypochlorite is added drop by drop.

W. T.

**Test for Free Sulphur.** By J. C. GIL (*Zeit. anal. Chem.*, 33, 54—55).—On adding an alkali polysulphide, or a solution of sulphur in an alkali hydroxide, to hot alcohol, which has been boiled long enough to expel all air, a blue colour is gradually developed. On cooling the blue colour disappears; it is, however, restored by reheating, if oxygen, or any other substance which decomposes polysulphides, has been expelled, otherwise not. 0.4 milligram of *hepar*

*sulphuris* will colour 50 c.c. of 96 per cent. alcohol. To use the test for the detection of free sulphur, the substance is added to boiling alcohol containing a trace of potash. M. J. .S.

**Toxicological Detection of Phosphorus.** By J. v. D'HAGEN and P. WOLTERING (*Chem. Centr.*, 1893, ii, 1103—1104; from *Ned. Tydschr. Pharm.*, 5, 335—343).—The authors mention a case of supposed phosphorus poisoning in which the phosphorus could not be proved by *post-mortem* appearances, or by the conventional chemical analysis. On distilling, however, the contents of the large intestine in a current of carbonic anhydride, gases containing phosphorus were given off. The authors did not venture to decide whether or no these gases were caused by a putrefactive process. L. DE K.

**Toxicological Detection of Phosphorus.** By H. W. BETTING and F. C. E. v. EMBDEN (*Chem. Centr.*, 1893, ii, 1104; from *Ned. Tydschr. Pharm.*, 5, 343—345).—The authors failed to detect phosphorus in the body of a man eight days after death. Traces of hypophosphorous acid and hydrogen phosphide could, however, be detected in every distillate. As the deceased had been medically treated with hypophosphites, the finding of volatile phosphorus compounds did not positively point to a poisoning with phosphorus. To throw some light on the case, the authors carefully searched for arsenic, as this is nearly always contained in commercial phosphorus, but rarely, if ever, in hypophosphites. They succeeded in demonstrating the presence of arsenic in the fatty-degenerated liver. L. DE K.

**Employment of Ammoniacal Mercuric Cyanide in Quantitative Analysis.** By F. W. SCHMIDT (*Ber.*, 27, 225—238).—In the quantitative estimation of metals precipitated as sulphides much time is consumed in converting the sulphides into oxides by redissolving in acids and precipitating with alkalis; the author has, therefore, endeavoured to devise a method of bringing about this conversion in one operation. The first attempt consisted in heating the washed sulphide with an excess of precipitated mercuric oxide, but the results obtained in this way were always too high, the oxide formed invariably containing basic sulphate; the formation of the latter may be avoided by using, in place of the oxide, a mixture of 1 part of mercuric nitrate and 2 parts of mercuric oxide, and the results then obtained in the case of copper and zinc sulphides agree very closely with the theoretical numbers.

A much more convenient method is to treat the moist sulphide with a cold saturated solution of mercuric cyanide in ammonia; the metallic sulphide is thus converted into cyanide with simultaneous formation of mercuric sulphide, and on ignition the latter is volatilised, and the cyanide decomposed, leaving the metal, which is converted into oxide by the oxygen of the air. The moist sulphide and filter are placed in a weighed crucible, the whole just covered with the ammoniacal mercuric cyanide solution, carefully evaporated to dryness, and ignited. The results obtained in the case of copper,

zinc, bismuth, and iron show a very close agreement with the calculated numbers.

Ammonia and mercuric cyanide combine to form the crystalline compound  $\text{Hg}(\text{CN})_2 \cdot \text{NH}_3$ , and when this is heated alone, it, unlike mercuric cyanide, does not yield any difficultly volatile paracyanogen, so that no error from this source is to be feared. The commercial mercuric cyanide should be recrystallised two or three times before dissolving in ammonia; or the amount of non-volatile matter in the solution may be determined and allowed for. H. G. C.

**Volumetric Estimation of Calcium, Strontium, or Barium.** By VIZERN (*J. Pharm.*, [5], 28, 442—443).—The neutral solution of the salt is titrated with a standard solution of sodium carbonate, using phenolphthalein as indicator. The process cannot be used in presence of other bases giving precipitates with carbonates.

W. T.  
**Estimation of Lead.** By LINDEMANN and MOTTEU (*Bull. Soc. Chim.*, [3], 9, 812—819).—Metallic sulphides are completely peroxidised by bleaching powder solution, the sulphur being oxidised to sulphate. Since peroxides in the presence of hydrochloric acid liberate their equivalent of iodine from potassium iodide, their amount may be estimated volumetrically.

In the case of galena free from foreign metals, the powdered mineral (0.5—1.0 gram), moistened with bleaching powder solution, is ground into an extremely fine mud, more bleaching powder solution (30—40 c.c.) is added, and then dilute hydrochloric acid (5 per cent.), gently warming until the liberated oxides are dissolved, the slow evolution of chlorine ensuring the oxidation of the last traces of sulphates. Enough bleaching powder solution to completely peroxidise the lead is now added to the product, and the peroxide collected, purified, and treated with excess of potassium iodide (25 c.c. of 5 per cent. solution) and hydrochloric acid (30 c.c. of 20 per cent. acid). The liquid is diluted (to 150—200 c.c.), and, after due agitation, the liberated iodine is titrated with sodium thiosulphate. 2 mols. of thiosulphate are equivalent to 1 atom of lead.

In the presence of metals other than copper, the lead is best precipitated as sulphide from the product of the action of bleaching powder on the mineral, and the sulphide treated as above. In the presence of copper, the copper sulphide simultaneously precipitated may be removed by means of potassium cyanide.

Lead carbonate and oxides are converted into the nitrate before treatment. The basic and peroxide oxygen of red lead may be estimated by treating it with nitric acid (sp. gr. 1.2). The undissolved peroxide and dissolved monoxide are then separately estimated; the total lead may also be estimated as a check.

Numerous results are quoted, which agree well amongst themselves, and fairly well with those obtained by the sulphate gravimetric method. JN. W.

**Quantitative Analysis by Electrolysis.** By A. GLASSEN (*Ber.*, 27, 163—165).—Lead is precipitated as dioxide, and a reguline  
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deposit is obtained in the presence of a sufficient quantity of nitric acid. The solution is warmed to 50–60° and a current of 1.5–1.7 ampères employed. About 1.5 grams of dioxide can be precipitated in three hours. If lead and copper are present in the same solution, 98–99 per cent. of the lead is precipitated in one hour with a current of 1.1–1.2 ampères. The current is then stopped, and the solution washed into another platinum dish, ammonia added, and the cold mixture electrolysed with a current of 1–1.2 ampères, when the copper, together with the remainder of the lead, is precipitated in about 3–4 hours. E. C. R.

**Quantitative Analysis by Electrolysis.** By O. PILOTY (*Ber.*, 27, 280–282).—In view of the adverse criticism to which Classen's electrolytic methods of quantitative analysis have been recently subjected, the author publishes a table of the experimental results obtained by him with these methods, showing that a high degree of accuracy can be thus attained. A. H.

**Analysis of Steel.** By L. SCHNEIDER (*Chem. Centr.*, 1893, ii, 623–624; from *Österr. Zeit. Berg. Hütt.*, 41, 365–368).—*Estimation of Sulphur.*—The author dissolves the sample in hydrochloric acid and passes the hydrogen sulphide through a solution of potassium permanganate. No sulphur is detectable in the residue. It is not advisable to expel any air from the apparatus by means of hydrogen, as this gas is difficult to free from sulphur. *Estimation of Silicon.*—As no silicon hydride is formed on dissolving steel in hydrochloric acid, the residue from the sulphur estimation may be safely used for the silicon estimation. The author does not follow the old plan of evaporating to dryness and taking up again with hydrochloric acid, but evaporates the liquid with sulphuric acid until sulphuric fumes appear. The residue is boiled with water until all the ferric sulphate has dissolved, and, after the silicic acid has been collected, ignited, and weighed, it is evaporated with hydrofluoric acid to ascertain its purity. L. DE K.

**Colorimetric Estimation of Small Quantities of Vanadium in the Presence of Large Quantities of Iron.** By V. v. KLEOKI (*Zeit., anorg. Chem.*, 5, 374–380).—With the aim of finding an easy method of determining vanadium in the presence of excess of iron, the author has investigated the action of a large number of reagents on vanadium solutions. A sulphuric acid solution of vanadic acid was employed. A large number of substances giving coloured compounds with vanadic acid also give colorations with iron salts, and are, therefore, useless for this purpose. Another class of substances (such as papaverine, meconine, quinine sulphate, &c.) give colour reactions with vanadic acid and not with iron, but the tint and degree of colour depend so much on degree of dilution, temperature, &c., as to be of little value. Dextrose appears to be the only substance that answers at all for this purpose. With greatly varying strength of acid, the colour varies with this between blue and green. If, however, the solution is made to contain only about 10 per cent.

of sulphuric acid, a pale green coloration is obtained, which varies approximately with the quantity of vanadium present, and forms a useful rough mode of estimation. It is not, however, very delicate, and the limit of error may reach as much as 8 per cent. of the vanadium present.

L. T. T.

**Separation of Vanadic acid from Chromic acid.** By V. v. KLECKI (*Zeit. anorg. Chem.*, 5, 381—382).—The author finds that a modification of Carnot's method of estimation of vanadic acid by precipitation as ammonium uranium vanadate (Abstr., 1887, 897) forms a good means for the separation of vanadic from chromic acid, the corresponding chromium precipitate being dissolved by the addition of even a single drop of acetic acid. Excess of uranium nitrate is added to the neutral solution containing the vanadic and chromic acids. A few drops of acetic acid are then added, the whole boiled, and filtered. The precipitate, after strong ignition, is weighed as  $V_2O_5 \cdot 2UO_3$ . Very good results are obtained.

L. T. T.

**Detection and Approximate Estimation of Sand in Food Stuffs, Meal, &c.** By A. EMMERLING (*Zeit. anal. Chem.*, 33, 46—48).—A solution of 1000 parts of crystallised zinc sulphate in 725 parts of water has, at ordinary temperatures, a sp. gr. of 1.43. A test tube is half filled with this solution and then filled nearly to the top with water, without admixture of the two layers. The substance to be tested is stirred into the water without disturbing the heavy liquid. The organic substances sink only to the surface of the zinc solution, the sand to the bottom of the tube.

For quantitative purposes, a special funnel-shaped vessel is used, to the neck of which is attached, by caoutchouc tubing, a graduated tube, each of whose divisions contains 0.2 gram of sand. The funnel is 10 cm. diameter at the top and has an angle of  $35^\circ$ , with a cylindrical neck 17 cm. long and 3 cm. diameter, tapered at its lower end at an acute angle to the diameter of the graduated tube. It is filled with the zinc solution to the top of the cylindrical neck, water is added nearly to the edge of the funnel, and 20 grams of material is used for each experiment, so that each division of the graduated tube corresponds with 1 per cent. of sand. In the event of the presence of calcium carbonate, the contents of the graduated tube can be treated with acid, washed, incinerated, and weighed.

M. J. S.

**Spirit Assaying by Weight.** By J. SCARISBRICK (*J. Soc. Chem. Ind.*, 12, 893—901).—The author has constructed tables which are suitable for use with a gravity bottle or any other instrument capable of ascertaining specific gravities from 1.000 to 0.790. They have been built from the invaluable material of Gilpin and Blagden; but, for spirits of great alcoholic strength, the numbers obtained by Tralles, Fownes, Drinkwater, and Squibs have been utilised. For the standard alcohol, Sikes's proof spirit at  $15.5^\circ$  has been adopted. The general principle proceeded on in building up the system is the recognition of weights and not volumes, as weight does not change with temperature, but volume does, particularly in the case of alcohol.



The system proposed by the author answers for the purpose of identifying the spirit, is easily understood, and quickly applied, furnishes accurate numbers for assessment at all temperatures, and satisfies the wants of all concerned.

L. DE K.

**Detection of Glucose and Cane Sugar in Honey.** By O. HAENLE (*Zeit. anal. Chem.*, 33, 99—103). Genuine honey from flowers contains no dextrin, or only traces; it rotates the plane of polarised light to the left. A dextrorotatory specimen is adulterated with starch-sugar syrup if it exhibits the dextrin reaction, but with cane sugar if dextrin is absent.

The honey from conifers, which is always brown, contains dextrin; before dialysis it rotates the plane of polarised light to the right; after dialysis it is optically inactive. A suitable dialyser for the removal of the diffusible constituents is figured and described. It consists of a shallow, wooden box, in which the tray of parchment paper is supported on parallel laths, whilst a slow stream of water flows below it. To detect dextrin, a solution is made of 1 part of the honey (first clarified by warming and stirring) in two parts of water. This solution is decolorised by warming for five minutes with 2 per cent. of animal charcoal. 5—10 c.c. is placed in a test tube and covered with a layer (2 c.c.) of absolute alcohol. A turbidity at the zone of contact indicates dextrin. Although the author's own numbers show that the optical rotation of pure honey is not constant, he gives the following formulæ for determining the amount of adulteration.

$$\text{For starch sugar in honey from flowers, } x = \frac{3P + p}{10}.$$

$$\text{For „ in honey from conifers, } x = \frac{3P - p}{10},$$

where P is the rotation of the honey solution, (1:2), p is the rotation of genuine honey (= 30), and x is the percentage of starch sugar syrup. For cane sugar syrup the divisor 10 is replaced by 4.

The validity of the author's conclusions is, however, disputed by numerous investigators.

M. J. S.

**Test for "Saccharin" in Presence of Salicylic acid.** By HAIRS (*Chem. Centr.*, 1893, ii, 987; from *Apoth. Zeit.*, 8, 500).—The isolated mixture containing "saccharin" and salicylic acid is acidified with hydrochloric acid and then mixed with excess of bromine water, which causes the complete precipitation of the salicylic acid. The filtrate from the dibromosalicylic acid is freed from bromine by a current of air and then agitated with ether. The latter on evaporation with a few drops of sodium hydrogen carbonate, leaves a residue of "saccharin," which may be recognised by its sweet taste and other well-known reactions. The author made a successful test experiment with 0.1 gram of "saccharin" and 0.05 gram of salicylic acid dissolved in 200 c.c. of claret.

L. DE K.

**Estimation of Hydrogen Cyanide in Cherry-Laurel Water, &c.** By G. DENIGÈS (*J. Pharm.*, [5], 29, 10—15).—When aqueous hydrogen cyanide is titrated with silver nitrate, the silver cyanide re-dissolves so slowly, especially in dilute solutions, as to obscure the end of the reaction; whilst when the acid is previously neutralised, the slightest excess of alkali retards the appearance of the final precipitate. These difficulties may be obviated by using potassium iodide as indicator, in solutions made strongly alkaline with soda or ammonia. With cherry-laurel water, for instance, the liquid (100 c.c.) is treated with ammonia (10 c.c.), and also with alcohol (5 c.c.) if hydrobenzamide be precipitated; a little potassium iodide is then added, and, finally, decinormal silver nitrate, until a distinct turbidity of silver iodide appears. The end-point is quickly and sharply determined: 1 c.c. of decinormal silver nitrate = 0.0054 gram of hydrogen cyanide. Hydrocyanic acid is neutralised with ammonia or soda, and sufficiently diluted before titration. Potassium cyanide is titrated in about 0.1 per cent. solution, with the addition of ammonia (10 c.c. to each 100 c.c.). Alkaline sulphides, if present, are first decomposed by ammoniacal zinc sulphate. The test analyses quoted are satisfactory. JN. W.

**Estimation of Hydrocyanic acid.** By G. GREGOR (*Zeit. anal. Chem.*, 33, 30—45).—When estimating gravimetrically as silver cyanide, the precautions to be observed are that the measured quantity (50 c.c.) of the liquid (bitter-almond, or laurel water, or a solution of the acid itself, so far diluted that no loss from volatilisation will occur during the measuring out) is mixed in a stoppered bottle, first with 5 c.c. of 1.73 per cent. ammonia, and then with a very small excess of silver nitrate solution. Nitric acid is then added to very feeble acidity. Since acid of 0.6 per cent. already dissolves traces of silver cyanide, this degree of acidity must not be exceeded. All the above operations must be performed in the cold, and with the greatest rapidity; a delay of a few minutes causes a loss in the result. Water is added to 200—300 c.c., the precipitate caused to aggregate by shaking, washed, dried, and ignited.

Of volumetric methods, Liebig's, Vielhaber's, and C. Mohr's, have, in the author's as in other hands, given higher numbers than the gravimetric. Volhard's method, carried out as follows, gives results closely agreeing with those obtained by weighing. 100 c.c. of the solution is mixed in a  $\frac{1}{4}$ -litre flask with 5 c.c. of ammonia, 50 c.c. of N/10 silver nitrate is added, and then immediately nitric acid, free from nitrous acid, to slight acidity. After making up, and shaking, 50 c.c. of the filtrate, mixed with a few drops of ferric sulphate, and, if necessary, with more nitric acid, is titrated with N/10 thiocyanate. M. J. S.

**Extraction of Fat.** By L. GEBBE (*Landw. Versuchs Stat.*, 1898, 193—206).—The author first shows that the usual method of estimating fat in fodders is not trustworthy, by reason of the dissolution of substances other than fat by the ether. He then recounts his experiments, wherein he mixed gypsum and bone charcoal with the substance to be analysed, the results not being wholly satisfactory;

finally he used Spanish earth, a red-brown powder containing chalk, but the latter must be removed, otherwise lime salts of the fatty acids would be formed—for this purpose the earth is levigated with water on a large porcelain dish, sulphuric acid is added, and the mass then thoroughly dried; the hardened mass is afterwards broken up and passed through a sieve with  $1\frac{1}{2}$ —2 mm wide mesh, and then heated to redness in a platinum basin.

Five grams of the substance are then mixed with 10—15 grams of the earth and placed in the extraction tube over a plug of wadding fitted into a narrowing of the lower part of the tube; this tube should be 14 cm. long, of which the upper 8 cm. are 2.5 cm. wide, the remainder 1 cm., the whole terminating in a still narrower tube, 2 cm. long; it is at the top of this last that the plug of wadding is placed. The ether which percolates is colourless, and leaves a colourless residue on evaporation, except when chlorophyll is present in the substance. To obtain good results, it matters not whether the ether be dry or not, but the substance itself must be air-dried only. E. W. P.

**Comparison of the Various Methods in Use for the Estimation of Milk Fat.** By GRAFFENBERGER (*Landw. Versuchs Stat.*, 1893, 247—252).—The various methods in use have been carefully examined, and the author points out the defects of each; he seems to consider Soxhlet's the most exact, as he has used that as the criterion for all the others—all give too low results. Apart from Soxhlet's, Schmidt's and Gottlieb's are the best, whilst Gerber's method is the worst. Schmidt's and Gottlieb's tally well with one another, but Schmidt's is the most rapid to work. Gerber's and Demichel's can only be considered to be preliminary methods; consequently, the author recommends the methods of Schmidt and Gottlieb as being, taking everything into consideration, exact, the most rapid, and the cheapest. E. W. P.

**Estimation of Ergot in Meals and Brans.** By H. LAUCK (*Landw. Versuchs Stat.*, 1893, 303—305).—10 grams of the sample is mixed with 20–30 c.c. of ether which has been distilled over sodium; then, after the addition of 1.3 c.c. of 5 per cent. sulphuric acid, and thorough shaking, the mixture is allowed to remain for six hours, after which it is filtered, washed with ether, and the filtrate made up to 40 c.c. in a test tube, or cylinder, marked at the 40 c.c. It is then mixed with 1.8 c.c. of a saturated solution of sodium hydrogen carbonate, when, after thorough mixing, a violet-coloured portion separates at the bottom of the tubes, and the percentage of ergot present is estimated by the depth of the tint produced. Standard tints are prepared beforehand. Ergot loses its colour by age.

E. W. P.

**Estimation of Urea.** By E. RIEGLER (*Zeit. anal. Chem.*, 33, 49—53).—Urea is decomposed by Millon's reagent, with evolution of equal volumes of carbonic anhydride and nitrogen. The theoretical volume of gas for 1 gram of urea is 74.4 c.c. (at 0° and 760 millimetres), but the average of numerous experiments gives 72.4 c.c.,

with such small variations that, by applying the corresponding factor the error will not exceed 0.5 per cent. The decomposition is effected in an ordinary test tube ( $6 \times \frac{3}{4}$  in.), 1 c. of the urea solution being taken. The reagent is prepared by dissolving 10 c.c. of mercury in 130 c.c. of nitric acid of 1.4 sp. gr., adding 140 c.c. of water, and, if necessary, filtering. Of this solution, 2 c.c. is run in by a funnel tube, and, when the first tumultuous evolution of gas is over, the mixture is heated to boiling several times. The gases are received in some form of gas volumeter and reduced to normal conditions, including the correction for aqueous vapour. The number of c.c. of gas, multiplied by the weight of 1 c.c. of nitrogen and by 1.1, gives the weight of urea in grams. M. J. S.

**Reactions with Potassium Mercuric Iodide, and with Iodine dissolved in Potassium Iodide.** By TANBET (*J. Pharm.*, [5], 28, 433—441 and 490—499).—*Reactions with alkaloids.*—The author summarises the work done on this group, and gives a table showing, for 19 alkaloids, the comparative delicacy of the reactions given by Mayer's, Valser's and Bouchardat's solutions. From numerous experiments of his own, he draws the following conclusions:—(1) Valser's solution precipitates the non-volatile alkaloids equally well from acid, neutral, or slightly alkaline, solutions. (2) The reaction is much more sensitive with the salts of the volatile alkaloids than with the free bases. (3) For some salts of volatile alkaloids—for example, pelletierine sulphate and cicutine hydrobromide, the delicacy of Valser's reagent is much increased by the addition of a little soda. (4) Valser's and Bouchardat's solutions should only be used to test neutral solutions, as many substances other than alkaloids are precipitated in acid solution.

Caffeine is not precipitated by potassium mercuric iodide from solution in organic acids. In sulphuric acid solution, Mayer's reagent shows the presence of one-fiftieth, Valser's, of one six-hundredth, part of alkaloid. Iodine in potassium iodide detects the presence of 1 part of caffeine in 20,000 parts of a mineral acid solution; with acetic acid, the reagent is useless.

Theobromine is not precipitated by potassium mercuric iodide, but gives a black precipitate with Bouchardat's reagent.

*Reactions with glucosides.*—No glucoside is precipitated by potassium mercuric iodide from neutral or acetic acid solution. From solution in dilute sulphuric acid, Valser's reagent precipitates vincetoxin, convallamarin, aurantiamarin, digitalein, and amorphous digitalin (Codex).

The combination of glucoside and mercuric iodide is soluble in alcohol; ether dissolves the digitalin compound and decomposes the others.

*Reactions with proteids, &c.*—Albumin gives a precipitate with potassium mercuric iodide in acetic acid solution. This precipitate is insoluble in excess of the reagent, in acetic acid, alcohol, ether, or solution of potassium iodide. For the detection of albumin in urine, 5 c.c. of the reagent is taken in a test tube, and the filtered urine added drop by drop. A bluish disc at the contact surface of the two

liquids is observed when the quantity of albumin per litre of urine is 0.01 gram or over.

In acid solutions, peptones give precipitates which show properties much resembling those of the alkaloid precipitates. Ether causes the disappearance of the precipitate from dilute solutions; more bulky precipitates collect into a sticky mass. In either case the ether decomposes the precipitate, and does not re-deposit the compound on evaporation, as is the case with most of the alkaloid precipitates. Peptones partially prevent the formation of precipitates with alkaloids in neutral solution, rendering the reaction much less delicate.

Solutions of 1 part of gelatin in 180,000 react with potassium mercuric iodide in acid solution. The reaction is less sensitive with iodine in potassium iodide. The mercurial precipitate is insoluble in ether, but soluble in alcohol and in hot acidified water. The gelatin precipitate collects together, forming a characteristically elastic mass.

An acetic acid solution of casein gives a precipitate with potassium mercuric iodide which is insoluble in excess of the hot reagent, but soluble in alcohol.

W. T.

**Separation and Estimation of the Cacao Alkaloids.** By W. E. KUNZE (*Zeit. anal. Chem.*, 33, 1—29).—The processes hitherto employed (see Abstr., 1893, ii, 198) have been directed exclusively to the estimation of the theobromine, whilst ignoring altogether the presence of caffeine, and the wide divergences between their results may in part be attributed to the fact that in some of the methods both alkaloids would be obtained, whilst in others the caffeine would be more or less perfectly excluded. The following method, based on proof tests at each stage, estimates both alkaloids. 10 grams of the cacao is boiled for 20 minutes with about 150 c.c. of 5 per cent. sulphuric acid, and the soluble matters are thoroughly washed out with boiling water. The warm extract is precipitated with a large excess of phosphomolybdic acid, and, after 24 hours, the precipitate is collected and washed with about a litre of 5 per cent. sulphuric acid. The filter containing the moist precipitate is treated in a beaker with excess of baryta in the cold, and carbonic anhydride is passed through the solution until all the baryta is thrown down. The whole is then thoroughly dried on the water-bath and extracted with boiling chloroform; the chloroform is distilled off, and the two alkaloids are left as a perfectly white residue, containing only a negligible trace of ash. The residue is weighed, dissolved in ammonia, and the solution heated to boiling. A considerable excess of silver nitrate (about 1.3 parts of silver for 1 part of theobromine) is added, and the boiling is continued until ammonia no longer escapes, and the liquid is reduced to a few cubic centimetres. Under these circumstances, an insoluble silver substitution-product of theobromine,  $C_7H_7AgN_3O_2$ , is obtained, whilst caffeine forms no such derivative, and remains wholly in solution. The precipitate is collected and washed with boiling water. The silver in it may either be determined by ignition or by dissolving in nitric acid and precipitating as chloride (in the latter method

the theobromine may be recovered from the filtrate for identification), but it is equally accurate and more rapid to employ a known excess of silver solution, and to estimate the excess in the filtrate by titration with N/10 thiocyanate solution (Volhard's method). Both the theobromine and caffeine can then be recovered by neutralising the respective nitric acid solutions, evaporating to dryness, and extracting with chloroform.

M. J. S.

**Estimation of Tannin.** By P. SISLEY (*Bull. Soc. Chim.*, [3], 9, 755—772).—Of the various processes devised for the estimation of tannin, those based on the precipitation by metallic salts or by gelatin are open to the objection that impurities are liable to be simultaneously thrown down, whilst that based on its oxidation by potassium permanganate is not available in the presence of organic impurities. If, however the tannin is first precipitated as the zinc salt, for instance, and the latter then oxidised with permanganate, trustworthy results may be obtained. The ammoniacal zinc acetate used for the precipitation is made by dissolving zinc oxide (40 grams) in hot dilute acetic acid (65 c.c. glacial acid, 50 c.c. water), and adding excess of ammonia (22° B. to 500 c.c.), the filtered solution being kept in a well-stoppered vessel. The tannin solution (50 c.c. of about 3.3 per cent.) is treated with the zinc solution (5 c.c.), and the precipitated zinc compound rapidly filtered and washed with aqueous ammonia (3 per cent.), by which means the gallic acid and other impurities are eliminated. The temperature must not be raised, or gallic acid will be also precipitated. The portion of precipitate adhering to the sides of the precipitating vessel is dissolved in dilute sulphuric acid (50 c.c., 1 to 5), and the remainder washed with this solution into a large porcelain basin (2 litres), and diluted to 1 litre with water. Indigo-carmin solution (50 c.c. of a 20 gram per litre solution of 20 per cent. paste) is now added, and standard permanganate, N/100, run in slowly (one drop per second to one drop per three seconds) until the colour of the liquid changes from green to dirty yellow. The titre of the solution having been determined by a separate experiment, the amount of tannin present can be calculated, since the amount of permanganate required to oxidise 63 grams of crystallised oxalic acid is capable of oxidising 41.57 grams of tannin. The process gives good results if the above details are closely adhered to, trial experiments with pure tannin alone and mixed with gallic acid and extractive matters of barks having proved quite satisfactory.

Some analyses of tannin-containing materials are given. Commercial tannin contains from 85 to 72 per cent. of tannin, Chinese gall nuts from 61 to 57 per cent., other gall nuts from 69 to 54 per cent., sumach from 19 to 12 per cent., and various commercial extracts of gall nuts and sumach from 44 to 12 per cent. JN. W.

**Estimation of Indigotin in Indigo.** By F. ULZER (*Chem. Centr.*, 1893, ii, 597; from *Mitt. Technol. Gewerb.-Mus. Wien*, 1892, 215).—The author's method is independent of the other organic matters which accompany the indigotin, and therefore yields good results

even in indigos of low percentage. About 1 gram of the very finely-powdered sample is boiled for 10 minutes with 50 c.c. of 5 per cent. aqueous soda and 10 c.c. of hydrogen peroxide (concentration not given). After cooling, it is diluted to twice its volume with water, and filtered through a tared filter. The precipitate is washed with hot water, then with dilute hydrochloric acid (1:10), again with hot water, and finally with boiling alcohol until the filtrate is pale blue. The precipitate is then dried at 100°, weighed, and incinerated, in order to weigh and subtract the small amount of ash. If the alcoholic filtrate is evaporated to dryness, and the residue heated at 100° until constant, the amount of indigo-red is approximately found. Good indigo contains about 70 per cent. of indigotin and 3 per cent. of indigo-red. A. H.

**Estimation of Alizarin and Allied Colouring Matters.** By W. P. DREAPER (*J. Soc. Chem. Ind.*, 12, 977—979).—1 gram of the alizarin paste or 0.25 gram of the powder is put into a small flask and, after adding 10 c.c. of a solution of sodium acetate (100 grams of the salt in a litre of water and 5 c.c. of acetic acid), the solution is roughly made up to 50 c.c. and mixed with 1 gram of barium sulphate. The flask is heated on a sand bath, and as soon as the liquid begins to boil, a solution of copper sulphate containing 0.0095 gram of copper oxide per c.c. is run in from a burette, until precipitation is complete. To test whether sufficient copper solution has been added to precipitate all the dye as copper lake, the end of a glass rod is from time to time dipped into the liquid and gently pressed on to a folded slip of filter paper, the slip afterwards being unfolded, and the under surface tested with potassium ferrocyanide.

The process will allow of the direct comparison of different samples by a numerical copper-oxide standard. Its accuracy is not likely to be disturbed by impurities other than substances that form colour lakes. Any reducing sugars will have no action, owing to the acid reaction of the solution. L. DE K.

**Detection of Copper Phyllocyanate in Green Preserves.** By A. TSCHURCH (*Zeit. anal. Chem.*, 33, 103).—An alcoholic extract is evaporated to dryness, the residue washed with water, and then treated with concentrated hydrochloric acid. Pure chlorophyll gives a deep blue solution and a residue soluble, with brown colour, in ether, but, if copper phyllocyanate is present, the hydrochloric acid dissolves only a small quantity of a yellow substance, and the residue dissolves, with green colour, in alcohol. If dilute hydrochloric acid is added to the alcoholic extract, a green colour indicates copper, since, in its absence, the mixture is yellow. M. J. S.

**Action of Sodium Peroxide on Natural or Artificial Colouring Matter of Wines.** By RUIZAND (*J. Pharm.*, [5], 29, 17—19).—When sodium peroxide is added to red wine, oxygen is evolved at a rate proportional to the acidity of the wine, and the colour changes through dark maroon to pale yellow. Any precipitate produced by

the liberated sodium hydroxide is easily soluble in acid. The time required to effect decolorisation varies with the relative amount of sodium peroxide, from five minutes with 0.25 gram per 5 c.c., to five days with 0.01 gram, whilst with 0.005 gram per 5 c.c. decolorisation is incomplete after eight days. The process is slightly hastened by the addition of hydrochloric acid. The same results are obtained with a tartaric acid alcoholic solution of cœnin, the colouring matter of red wine.

Aniline and azo-dyes, such as are used in the sophistication of wine, are not affected by the peroxide in acid solution, so that their presence in wine may be detected by treating it (5 c.c.) with sodium peroxide (0.1 to 0.15 gram) for 20 minutes, and then acidifying with acetic acid. If the colour is not discharged, an artificial dye is present, and, since the natural colouring matter of the wine has been destroyed by the reagent, may be tested for in the usual way. Other vegetable colouring matters behave in the same way as the colouring matter of wine, and cannot be detected by this means. JN. W.

**Detection of Bile Pigment in Urine.** By A. JOLLES (*Zeit. physiol. Chem.*, 18, 545—557).—In addition to the well-known Gmelin's test for bile pigment in urine, there are several modifications and several other tests. In all, twenty are described in the present paper, and their relative delicacy ascertained. Of these, some half dozen are so little adapted to the purpose that it is necessary to add 10 per cent. of bile to the urine in order to obtain them; and only one (Rosenbach's) of the six modifications of Gmelin's test is as delicate as the original. This requires 5 per cent. of bile. Two out of the list are so delicate as to be given by 2 per cent. of bile. Of these, Rosin's test is one (*Berlin klin. Wöch.*, 1893, 106), and Hupperts' (*Arch. Heilk.*, 8, 351, 476, 1887) the other.

Rosin's test consists in the grass-green ring, which appears on pouring dilute iodine tincture carefully on the surface of the urine.

Huppert's test is as follows:—8 to 10 c.c. of urine is precipitated with milk of lime and the precipitate collected; the latter is then treated in a test tube with alcohol containing sulphuric acid, and the acid liquid heated to boiling, when it becomes green or blue if bile pigment is present. W. D. H.

**Estimation of Urobilin in Urine.** By A. STUDENSKY (*Chem. Centr.*, 1893, ii, 668; from *St. Petersburger med. Wöch.*, 1893, 283).—The process consists in extracting the urobilin by means of chloroform in the presence of copper sulphate and ammonium sulphate, and in the colorimetric comparison of the coloured chloroform solution of urobilin with standard solutions. If the urine to be examined be shaken with chloroform in the presence of copper sulphate, the urobilin will not be entirely dissolved until after repeated shakings. If, however, after the addition of the copper sulphate, the urine be saturated with ammonium sulphate, which, according to Méhu, precipitates urobilin, the whole of the latter is at once taken up by the chloroform. Without copper sulphate, only a portion of the urobilin is dissolved. The process is carried out in



the following way:—20 c.c. of urine is treated with  $\frac{1}{10}$  vol. of saturated copper sulphate solution, then saturated with crystallised ammonium sulphate, and 10 c.c. of chloroform added. The mixture is shaken for some minutes, and as soon as a copper-red layer of chloroform solution has settled, a portion of it is removed by a separating funnel, placed in a test-tube, and compared with a standard solution of urobilin in chloroform. This solution is prepared by extracting a considerable amount of urine which contains much urobilin in the manner described, evaporating the chloroform solution to dryness, washing with ether, and weighing the residue. A series of solutions is then made up from this residue, and these may be preserved, even as long as two months, if kept in the dark in closed vessels and covered by a layer of saturated solution of ammonium sulphate.

A. H.

**Estimation of Albumin.** By F. KLUG (*Chem. Centr.*, 1893, ii, 499).—For the estimation of albumin, the author mixes 2 c.c. of the liquid to be examined with concentrated aqueous soda, and adds 4 drops of a 10 per cent. copper sulphate solution. The carefully-filtered solution is then examined in a spectrophotometer, and the intensity of the biuret coloration determined. The results obtained are trustworthy, and the whole estimation may be made in a quarter of an hour. The estimation of albumin in urine may also be carried out in this manner as by means of an excess of copper sulphate the greater part of the colouring matters are precipitated. The amount of colouring matters may also be determined by Vierordt's method, and deducted from the total amount of colouring matter and albumin found by the author's method.

H. G. C.

**Detection of Albumin in Urine.** By A. OLLENDORFF (*Zeit. anal. Chem.*, 33, 120—121).—The author confirms the value of Zouehlos' potassium thiocyanate test. It is capable of detecting 0.005 per cent. of albumin, and other constituents of urine, with the exception of propeptone, have no disturbing influence.

After taking copaiba balsam, or sandal oil, the urine may contain resin acids, precipitable by nitric acid, and, therefore, liable to be mistaken for albumin. Treatment of the precipitates with alcohol fails to distinguish them, since both dissolve. Alexander recommends the use of the following tests:—2 or 3 drops of hydrochloric acid are added to 8—10 c.c. of urine; this precipitates the resin acids. If, on adding acetic acid, a precipitate is produced not soluble in excess, this consists of mucin. A sample is heated and mixed with one-third of its volume of nitric acid (strength not stated). Since both resin acids and mucin are redissolved under these conditions, a turbidity indicates albumin.

M. J. S.

## General and Physical Chemistry.

**Spectrum of Electrolytic Iron.** By J. N. LOCKYER (*Proc. Roy. Soc.*, 54, 359—361).—A series of photographs was taken of the part of the spectrum between the K and C Fraunhofer lines. Electrolytic iron of a very high degree of purity was employed, and the spectrum obtained by using this as the poles of an electric arc lamp. The results are compared with those previously obtained by Thalen, Kayser and Runge, and McClean, the agreement being in all cases satisfactory. Many lines occur in the spectra of the other observers, however, which are not indicated in these photographs. In many cases, they are probably due, and can be traced, to impurities in the iron used by them; in other cases, however, they appear to be owing to differences in temperature, or to insufficiency of exposure of the photographic plates. Evidences were obtained of calcium and manganese in the specimen of electrolytic iron employed, as well as of very minute traces of other metals.

L. M. J.

**Refractometric Researches.** By J. F. EIJKMAN (*Rec. Trav. Chim.*, 12, 268—285).—In a previous paper (*Abstr.*, 1893, ii, 1), the author has shown that it is impossible to calculate correctly the molecular refractions of the initial terms of any homologous series making use of the atomic refractions deduced in the ordinary manner, although a constant difference exists between the refractions of the higher members of such a series, and this difference is equal to that observed in any other similar series. It is now shown that the dispersion is subject to like irregularities. It therefore appears that the molecular refraction of the variable term in any homologous series, say  $-\text{CH}_2-$ , is constant and independent of the character of the series; and it would seem probable that, in like manner, the invariable end terms of the series have constant molecular refractions, independent of the nature of the series; or, in other words, in any series  $x(\text{CH}_2)_m$ ,  $y(\text{CH}_2)_n$ , and  $z(\text{CH}_2)_p$ ; the refractions for  $\text{CH}_2$ ,  $x$  and  $y$  should be constants, and, when once known, the refractions of any term of a series of this form might be calculated. The author shows that, neglecting the initial terms of the series, the above supposition is correct, and that an excellent agreement between calculated and observed values for the molecular refractions can be obtained. Tables are given for the values of the refractions of different groups entering into the composition of homologous series.

H. C.

### Relation of the Critical Coefficient to the Formula $\frac{n-1}{d}$ .

By R. NASINI (*Gazzetta*, 23, ii, 576—587).—The relation between the refraction constants of a substance and its critical coefficient,  $k$ , or the ratio of its critical temperature expressed on the absolute scale, and its critical pressure, has been already indicated by Guye

(*Ann. Chim. Phys.*, [6], 21, 206). He showed that  $M = 1.8 k/R$ , where  $M$  and  $R$  are respectively the molecular weight and the specific refraction for the ray of infinite wave-length calculated from the formula  $\frac{n^2 - 1}{d(n^2 + 2)}$ . The molecular weight of a substance at its critical point can thus be determined, and was found by Guye to be in general the same as in the gaseous state. The same author further stated that the critical coefficient of a substance is the sum of the critical coefficients of the atoms composing its molecule; the nature of the bonds between the atoms has to be considered, just as in the case of molecular refraction.

If the refraction formula of Gladstone and Dale holds as well as that of Lorentz and Lorenz, the value  $\frac{M(A-1)}{kd}$  should be a constant;  $A$  being the refractive index for infinite wave-length given by Cauchy's formula. The author has calculated this constant for a number of aliphatic compounds, and finds it to have the mean value 2.79; the constancy is, however, not quite so good as that obtained from Guye's formula.

The author therefore considers that Gladstone and Dale's formula suffers but little from Guye's deduction of the  $n^2$  formula from the critical constants. W. J. P.

**Relation between the Refractive and Rotatory Properties of Compounds. New Method for Determining the Specific Rotation of Optically Active Substances.** By I. KANONNIKOFF (*J. pr. Chem.*, [2], 49, 137—184).—By determining the angles of the rotation of the plane of polarised light,  $\alpha_1$  and  $\alpha_2$ , and the angles of minimum deviation,  $\phi_1$  and  $\phi_2$ , of solutions of different concentration, it is found that  $\alpha_1 - \alpha_2/\phi_1 - \phi_2 = \text{constant} = A$ , from which the differential equation  $\frac{d\alpha}{d\phi} = A$  and the integration  $\alpha = A\phi \pm B$  result.

The author used a prism of 60° angle and a polarimeter tube of 200 mm. The values obtained for a large number of optically active substances dissolved in different solvents are tabulated.

The value of the constants  $A$  and  $B$  is independent of ultimate composition and of similarity of chemical properties. Thus, whilst lactose and nicotine give nearly the same value for  $A$ , galactose and glucose give very different values for the same constant.

The constants are of different value when the same substance is dissolved in different solvents, but the relation  $B/A$  is nearly the same for every substance dissolved in the same solvent; so that this relationship, which may be termed  $C$ , depends solely on the solvent employed. For example:—

	B.	A.	$\frac{B}{A}$ or $C$ .
Sucrose in water .....	268.23	11.40	23.52
Lactose       " .....	229.63	9.73	23.60
Nicotine       " .....	227.72	9.66	23.56
Nicotine in alcohol.....	537.50	20.77	25.87

By dividing the above integration by  $A$ , it becomes  $\alpha = A(\phi + C)$ . Obviously, the determination of the value of  $C$  for different solvents adds another physical constant to those already available for ascertaining the relationship between structure and properties. The author gives a table showing this value for 63 different substances which were used as solvents for camphor, and, in a few cases, other optically active substances. Certain deductions are made from this table, such as that the introduction of  $\text{CH}_2$  into a molecule increases the value of  $C$  for the compound by an amount varying from 0.46 to 1.35, and averaging 0.85; considerable deviation from the average is observed in the case of formic acid and methylic alcohol. The most important of these deductions is, in the author's opinion, that the value of  $C$  depends more on the constitution of the compound than on the number of the atoms in its molecule, and on the manner in which these are united. Since the last-named conditions are the chief factors on which the other physical properties of compounds depend, the new value will furnish a nearer insight into the relationship between constitution and properties than can the older constants.

The influence of double linking of carbon atoms on the value of  $C$  is next discussed, and the few values which have been obtained for aromatic compounds are correlated. The angle  $\phi$  decreases with dilution in the fatty series, but increases in the aromatic series; consequently the equation is  $\alpha = A\phi + B$ , and  $B$  becomes a positive value for compounds of the aromatic series. The value of  $C$  for these compounds diminishes with increase of complexity, but the value of the coefficient  $y$  (see below) increases with the increased complexity.

It is to be noted that for the determination of  $C$  it is a matter of indifference whether the optically active compound is the solvent or the substance dissolved.

When the relationship between the specific rotatory power of optically active substances and the constants  $A$  and  $B$  is examined, it is found that the values  $\frac{B}{[\alpha]_D}$  and  $\frac{[\alpha]_D}{A}$  are constants for the same solvents, whatever the dissolved substance, so that  $[\alpha]_D = Ax = B/y$ , where  $x$  and  $y$  are coefficients depending purely on the nature of the solvent. Obviously,  $C = xy$ .

By using the known values of  $[\alpha]_D$  for sugars,  $x$  and  $y$  are shown to be 5.60 and 4.20, respectively, for water. This new method for calculating the specific rotatory power is independent of a knowledge of the density and concentration of the solution. The coefficients  $x$  and  $y$  for the solvent being known, it suffices to determine the angles  $\alpha$  and  $\phi$  for a solution of the substance whose specific rotatory power is to be ascertained; to dilute this solution and again determine the angles  $\alpha$  and  $\phi$ ; these data will serve for the calculation. In the table, the value of  $y$  for a large number of compounds is given.

In applying this method, the author has found some notable exceptions in which the calculated  $[\alpha]_D$  is twice that which has been directly determined. For example, a solution of Russian turpentine in ethylic alcohol gives the values  $A = 5.40$  and  $B = 137.00$ ; the

values for  $\alpha$  and  $\gamma$  for ethylic alcohol being  $5.16$  and  $5.00$ , respectively,  $[\alpha]_D$  for this turpentine becomes  $27.63^\circ$ ; the observed value is  $[\alpha]_D = 27.89^\circ$ . But a solution of this turpentine in chloroform has  $A = 30.80$  and  $B = 999.79$ ; the values for  $\alpha$  and  $\gamma$  for chloroform are  $1.78$  and  $18.21$  respectively, whence  $[\alpha]_D = 27.43^\circ \times 2$ . Nicotine and coniine are also quoted as showing the same anomaly.

These cases remain unexplained, but some light on the subject has been gathered from a study of sugar solutions. It was found that whilst a number of inverted sugars gave the same values for  $[\alpha]_D$  as were calculated on the hypothesis that this value should be the mean of those of the various constituents into which the sugars are known to be converted by inversion, there were a few cases in which the determined value for  $[\alpha]_D$  was some multiple proportion of that calculated on the above hypothesis. Numerous experiments on mixtures of molecular quantities of sugars are quoted, and it is concluded that (1) the existing values for the specific rotatory power of sugars are inaccurate; (2) the specific rotatory power of a mixture of compounds in molecular proportion is the mean of the specific rotatory power of the constituents; and (3) in the cases in which the mean value of the specific rotatory powers of the constituents in such a mixture is a multiple or submultiple of the observed value, there has been an action between the constituents of the mixture (compare Berthelot's compound of dextrose and lævulose (Abstr., 1887, 24).

The last conclusion raises the question whether some dissociation or association may not explain the anomalous behaviour of Russian turpentine, nicotine, and coniine, referred to above. An investigation of tartrates also suggests a similar explanation. The following values for tartaric acid and metallic tartrates have been obtained:—

	$[\alpha]_D$ .
Tartaric acid .....	+12.46°
Acid tartrate, $C_4H_5RO_6$ .....	+24.48
Normal tartrates, $C_4H_4R_2O_6$ .....	+30.44

Normal tartrates of the amines, in aqueous solution, divide themselves into three classes: (1) those which have the same value for  $[\alpha]_D$  as have acid tartrates; these are the tartrates of the more powerful bases, such as ethylamine, and must be regarded as being dissociated in the solution into acid tartrates and uncombined amine; (2) those which have  $[\alpha]_D = 18^\circ$ , such as isobutylamine tartrate; these must be looked upon as being partly dissociated into acid tartrate and partly into free tartaric acid and free base; (3) those which have  $[\alpha]_D = 12^\circ$ ; these dissociate in water completely into acid and base, and comprise the tartrates of the feeble bases, such as aniline.

In alcoholic solution, the tartrates of the more powerful bases have  $[\alpha]_D = 30^\circ$ , and are, apparently, not dissociated. None of the tartrates which the author has examined are further dissociated in alcohol than is expressed by the specific rotatory power  $[\alpha]_D = 18^\circ$ .

A. G. B.

**Molecular Rotatory Polarisation.** By G. WYROUBOFF (*Ann. Chim. Phys.*, [7], 1, 5—90; compare *Abstr.*, 1893, ii, 106).—The rotatory polarisation of substances in the liquid, dissolved, or gaseous state is characterised as molecular, in contradistinction to the optical activity of solid substances, like quartz, which disappears on destruction of the crystalline edifice by fusion or solution. The supposition of a connection between enantiomorphous hemihedrism and circular polarisation is unjustifiable, so large a number of exceptional cases being known; thus, the enantiomorphous sodium strontium arsenite, and nitrates of lead and barium do not circularly polarise either in the crystalline or liquid state, whilst on the other hand very few optically active substances crystallise in enantiomorphous forms. The only relation which can at present be enunciated is, that optical antipodes exist of those substances which are optically active and show non-superposable hemihedrism. By varying the conditions of crystallisation of many alkaloid salts, either right- or left-handed crystals may be obtained, although, of course, the specific rotation remains unchanged in magnitude and sign.

The author gives the name of crystalline particles to the aggregates of chemical molecules which he supposes to persist when a crystalline substance is dissolved, fused, or volatilised; he quotes a number of facts in support of this view, and has verified the old observation of Frankenheim that the red and yellow modifications of mercuric iodide can be volatilised without change of colour; the vapour of the red modification is therefore not the same as that of the yellow (compare, however, Berthelot, this vol. ii, 94).

The author defines two substances as optically isomeric when their optic axial angles do not differ by more than  $10^\circ$ ; he then determines the connection between the specific rotations of substances in solution and the degree of their isomorphism.

Substances which are geometrically and optically isomorphous have the same specific rotatory powers. Quinidine crystallises with 1 mol. of the alcohols of the ethylic series; the compounds with methylic and ethylic alcohol are geometrically and optically isomorphous and have the same specific rotation. The rotation is calculated on the crystalline substance, since the crystalline particles which exist in the solution have the composition of the crystals. The same is true of the following sets of substances. Cinchonine hydrobromide with  $1\text{H}_2\text{O}$  and  $\frac{1}{2}\text{C}_2\text{H}_5\text{O}$ ; cinchonidine hydrobromide with  $\frac{2}{3}\text{H}_2\text{O}$ ,  $\text{MeOH}$ , and  $\frac{1}{3}\text{H}_2\text{O} + \frac{1}{2}\text{EtOH}$ ; cinchonidine hydriodide with  $\frac{2}{3}\text{H}_2\text{O}$  and  $\text{MeOH}$ ; cinchonidine combined with  $\text{HCl} + \text{MeOH}$  and  $\text{HBr} + \text{MeOH}$ ; the hydrates with  $5\text{H}_2\text{O}$  of strychnine sulphate and selenate; the hydrates with  $6\text{H}_2\text{O}$  of strychnine sulphate and selenate; strychnine sulphate and selenate with  $\text{EtOH}$ ; the salts of cinchonidine with  $\text{HBr} + \text{MeOH}$ ,  $\text{HBr} + \frac{1}{3}\text{H}_2\text{O} + \frac{1}{2}\text{EtOH}$ ,  $\text{HBr} + \frac{2}{3}\text{H}_2\text{O}$ , and  $\text{HCl} + \text{MeOH}$ .

The author has also examined fully the crystallographic and rotatory properties of two other large groups of salts of the alkaloids. The first group consists of those sets of substances which are geometrically but not optically isomorphous, whilst in the second group are placed those sets of salts which, although isomorphous among themselves, are not comparable in solution since they form different com-

pounds with the solvent; they may also dissolve without decomposition in one solvent but be partly decomposed on dissolving in another. No constancy of specific rotation was found in these cases.

W. J. P.

**Electrolytic Dissociation and Optical Rotatory Power.** By G. CARRARA (*Gazzetta*, 23, ii, 587—595).—The author has determined the specific rotation of nicotine in aqueous solutions of its hydrobromide, nitrate, and propionate; the value obtained in 8—9 per cent. solutions is  $+12.17^{\circ}$  to  $12.58^{\circ}$ . Nernst's law respecting optical activity and electrolytic dissociation is thus confirmed.

W. J. P.

**Alternate Current Electrolysis.** By J. HOPKINSON, E. WILSON, and F. LYDALL (*Proc. Roy. Soc.*, 54, 407—417).—The paper contains the results of a number of experiments, the object of which was to determine (i) the dissipation of energy due to *electrolytic hysteresis*, and (ii) the quantity of an ion per square centimetre of an electrode, necessary to change the properties of the electrode to that of the ion during alternate current electrolysis. The experiments were carried out by passing an alternating current through an ordinary non-inductive resistance and through an electrolyte, and then measuring the differences of potential at the extremities of these two resistances at different phases of the current. Curves of current and potential differences with different frequency are given, as well as curves showing the dissipation of energy per cycle. As a result of the experiments, it was found that with platinum electrodes of 150 sq. cm. area, the ion being hydrogen, the maximum electromotive force due to polarisation was reached when  $\frac{1}{10}$ th of coulomb had passed through the cell, that is, when 0.00001 gram of hydrogen had been liberated. It hence appears that 0.0000007 gram of hydrogen is sufficient to polarise 1 sq. cm. of platinum. Assuming the density of the hydrogen to be comparable with that of liquids, the thickness of the film of hydrogen necessary is of the same order as this number—0.0000007 cm.—a number comparable with the distance between the molecules.

L. M. J.

**Minimum Electromotive Force required for the Electrolysis of Salts of the Alkalis.** By C. NOURRISSON (*Compt. rend.*, 118, 189—192).—The author has observed and calculated the E.M.F. required to electrolyse a number of salts of the alkali metals. His results, given in volts, are contained in the following table.

	CL	Br.	I	SO <sub>4</sub> .	NO <sub>3</sub> .	ClO <sub>4</sub> .
Potassium.....	1.97	1.74	1.15	2.40	2.32	2.45
Sodium.....	2.10	1.71	1.19	2.40	2.36	2.42
Lithium.....	2.01	—	—	2.43	2.45	—
Calcium.....	1.95	1.71	1.16	—	2.28	—
Barium.....	1.94	1.72	1.17	—	2.37	2.48
Ammonium.....	1.83	1.46	—	2.29	—	—
Calculated values.....	2.02	1.75	1.16	2.15	2.07	2.07

The solutions compared contained the same number of equivalents

per unit volume. It is pointed out that the minimum E.M.F. required for the electrolysis of salts of the alkali metals in aqueous solution is constant for salts of the same acid.

H. C.

**Fusibility of Mixtures of Isomorphous Salts.** By H. LE CHATELIER (*Compt. rend.*, 118, 350—352).—The author regards all compounds as isomorphous which will crystallise together in proportions that vary continuously. The following table shows the melting points of saline mixtures, the composition of which is defined by the ratio of the total number of molecules in the mixture to the number of molecules of that salt which is mentioned second.

$K_2CO_3$ and $Na_2CO_3$ ...	{	0.0	0.20	0.38	0.55	0.65	0.79	1.0	
	t.	860	770	715	690	700	740	820°	
$Na_2SO_4$ and $K_2SO_4$ ...	{	0.0	0.11	0.14	0.20	0.33	0.50	0.75	1.0
	t.	860	830	825	815	830	855	940	1045°
$K_2CrO_4$ and $K_2SO_4$ ...	{	0.0	0.15	0.33	0.50	0.66	1.0		
	t.	940	950	960	985	1000	1045°		
$Na_2SO_4$ and $Na_2CO_3$ ...	{	0.0	0.33	0.50	0.67	0.78	1.0		
	t.	860	810	800	790	795	820°		
$K_2CO_3$ and $K_2SO_4$ ....	{	0.0	0.33	0.40	0.50	0.67	0.75	1.0	
	t.	860	880	900	920	960	980	1045°	
$NaCl$ and $KCl$ .....	{	0.0	0.42	0.45	0.50	0.74	1.0		
	t.	780	660	650	640	690	740°		
$KCl$ and $KI$ .....	{	0.0	0.17	0.33	0.50	0.67	0.80	1.0	
	t.	640	610	590	580	630	680	740°	

C. H. B.

**Variation of Molecular Surface Energy and Temperature.** By W. RAMSAY and J. SHIELDS (*Phil. Trans.*, 184, 647—673; compare *Trans.*, 1893, 1089).—In this paper, the authors give the experimental details of the method which they used later for determining the molecular weights of liquids from the variation of their surface tension with the temperature. The equation which expresses this variation accurately is  $\gamma s = \lambda \tau - \kappa d (1 - 10^{-\lambda \tau})$ , where  $\gamma$  is the surface tension,  $s$  the surface,  $\tau$  the temperature measured downwards from the critical temperature,  $d$  a constant difference of temperature (about 6°), and  $\kappa$  and  $\lambda$  constants. The factor  $1 - 10^{-\lambda \tau}$  practically vanishes when  $\tau$  is greater than 30°.

The liquids examined were ether, methylic formate, ethylic acetate, carbon tetrachloride, benzene, chlorobenzene, acetic acid, methylic alcohol, and ethylic alcohol, measurements being made as low as -90° when possible. The value of  $\kappa$  varies from 2.04 to 2.22 for the different substances, except the alcohols, which do not come under the above formula at all.

There is no angle of contact between liquid and glass when the liquid surface is in contact with its own vapour. Ordinary measurements of capillarity give inconstant results on account of the surface tension of the liquid itself not being measured, but rather the surface tension of a solution of air in the surface film of the liquid.

The results are given in tabular and curve form.

J. W.

**Combination of Sulphuric Acid with Water in the Presence of Acetic Acid.** By H. C. JONES (*Amer. Chem. J.*, 16, 1—19).—



The lowering of the freezing point of acetic acid by mixtures of sulphuric acid and water was determined and compared with the lowering produced when sulphuric acid alone or water alone was added to the acid. Evidence was thus obtained of the existence of the two hydrates,  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ , in acetic acid solution, but the results do not indicate the existence of any hydrates containing a larger quantity of water, even when as much as 37 equivalents of water are present to one of sulphuric acid. These hydrates are somewhat unstable in the acetic acid when their solutions are very dilute, and when the excess of water present is not very great. They can be regarded as dissociated under these conditions by the acetic acid into sulphuric acid and water.

Mixtures of ethylic alcohol and water were examined in the same way, but without obtaining any evidence of the existence of compounds of the two. In the case of dry sodium acetate and water, which were also examined, some combination appears to take place, but definite results were not obtained.

H. C.

**Diminished Solubility.** By F. W. KÜSTER (*Ber.*, 27, 324—328).—Nernst has shown that the solubility of one liquid in another with which it is partly miscible, is, when foreign substances are dissolved in it, diminished according to the same laws as regulate the diminution of its vapour pressure when the second liquid is not present. The experimental confirmation has been somewhat difficult to execute in a general manner on account of the limited choice of partially miscible liquids. The author has used phenol and a saturated aqueous solution of sodium chloride, and has obtained good results with these liquids. The constant  $k = \frac{L_0 - L}{L} \cdot \frac{g_1}{M_1} \cdot \frac{M_2}{g_2} \cdot \frac{V}{V_0}$ , has a mean value of 1.125,  $L_0$  and  $L$  being the solubilities in water of pure phenol and of phenol containing a foreign substance, respectively,  $g_1$  and  $g_2$  the weights of phenol and of the foreign substance,  $M_1$  and  $M_2$ , their molecular weights, and  $V_0$  and  $V$ , the volumes of phenol before and after addition of the foreign substance (compare next Abstract).

J. W.

**Titration Method of Determining Molecular Weights in Solutions.** By F. W. KÜSTER (*Ber.*, 27, 328—331; compare preceding Abstract).—Two separating funnels (100 c.c. capacity) are each charged with 25 c.c. of an aqueous solution saturated at the laboratory temperature both with sodium chloride and phenol, and also with 10 c.c. of phenol saturated by contact with a concentrated aqueous solution of sodium chloride. Into one of the funnels, a weighed quantity of the substance whose molecular weight is to be determined, is introduced. This substance must be soluble in phenol and very sparingly soluble in water. Both funnels are then shaken up for two minutes, care being taken not to heat the liquids by contact with the hand, after which they are allowed to settle for half an hour. A wad of cotton-wool is now inserted into the tube of each funnel, 1 c.c. of the liquid permitted to escape, and the rest of the filtered aqueous layer collected in a small well-corked flask. The phenol in

the aqueous solution is estimated by titration with bromine (*J. prakt. Chem.*, [2], 17, 390), 10 c.c. of the solution being introduced into stoppered bottles along with 25 c.c. of bromide-bromate solution and 10 c.c. of 10 per cent. hydrochloric acid. After half an hour, 10 c.c. of potassium iodide solution (42 g. per litre) is added, and the solution, after 15 minutes, titrated with N/20 thiosulphate solution.

The bromide-bromate solution is made by diluting the salts produced from 100 grams of sodium hydroxide and excess of bromine, first to 1 litre, and immediately before use to one-tenth of this strength.

The molecular weight of the foreign substance is calculated from the formula

$$M_s = 1.125 \cdot \frac{94}{10} \cdot \frac{L}{L_0 - L},$$

where the letters have the same signification as in the preceding abstract.

For benzene, the molecular weight as thus determined varied from 74.7 to 80.1 (theory = 78); for chloroform from 95.9 to 121.0 (theory = 119.5); for vinyl tribromide from 257.5 to 294 (theory = 267).  
J. W.

**The Volume Theory of Crystalline Substances.** By W. MUTHMANN (*Zeit. Kryst. Min.*, 22, 497—551).—The molecular volume of crystalline substances is, as is well-known, not altogether an additive property; the molecular volume cannot be accurately calculated from the atomic volumes of the elements concerned, if these are deduced from the densities of the solid elements. A number of instances, chosen from amongst metallic salts, are quoted, showing the very inaccurate results obtained by the application of Kopp's law.

Five out of the seven different known crystalline modifications of sulphur have molecular volumes varying from 14.98 to 17.1; similarly this constant varies from 16.43 to 18.43 for the three forms of crystalline selenium. The crystalline form of the substance must consequently be taken into account in any investigation of the molecular volume of solid substances. The author considers that in polymorphous substances the chemical molecules consist of the same numbers of atoms; most probably the different molecular volumes of the various modifications are conditioned by the different distances between the chemical molecules in the physical molecules, by the different distances between the physical molecules in the crystal, and by the different numbers of chemical molecules composing the physical ones.

If two substances are strictly isomorphous, that is, if they possess similar crystalline forms, and give mixed crystals—all of whose properties are proportional to the quantity of each constituent present—it may be assumed that the weights of the elements of the crystalline masonry of each are proportional to the equivalent weights of the substances concerned. This assumption, however, can only be made in cases of perfect isomorphism, and would not necessarily hold between potassium chloride and sodium chloride, the former being

asymmetrically hemihedral and cubic, and the latter being holohedrally cubic.

The relative size of the elements of the crystalline masonry can now be calculated. Let  $S_a$  and  $S_b$  be the specific gravities of two isomorphous substances  $a$  and  $b$  of molecular weight  $W_a$  and  $W_b$  respectively; let also the volumes of the elements of the crystalline structure be  $V_a$  and  $V_b$ , and the corresponding molecular volumes be  $M_a$  and  $M_b$ ; then

$$\frac{V_a}{V_b} = \frac{W_a S_b}{S_a W_b} = \frac{M_a}{M_b}.$$

Now, the element of crystalline masonry, according to the theory of crystal structure developed by Bravais and Sohncke, is a parallel-pipedon; in the tetragonal system, this parallel-pipedon has a square base and the ratio of the length of the side to the height is indicated by the ratio  $a:c$ , of the lengths of the crystallographic axes. Let the heights of the parallelopipeda in the two substances be  $\chi_a$  and  $\chi_b$ , and the lengths of the sides of the basal square be  $\omega_a$  and  $\omega_b$  respectively. Then a very simple calculation shows that

$$\frac{\chi_a}{\chi_b} = \sqrt[3]{\frac{c_b a_a M_a}{a_b c_a M_b}} \quad \text{and} \quad \frac{\omega_a}{\omega_b} = \sqrt[3]{\frac{a_b^2 c_a^2 M_a}{c_b^2 a_a^2 M_b}},$$

where  $a_a:c_a$  and  $a_b:c_b$  are the crystallographic axial ratios for the substances  $a$  and  $b$  respectively. Putting  $a:c = 1:m$  for any substance.

$$\chi : \omega = \sqrt[3]{\frac{M}{m}} : \sqrt[3]{Mm^2}$$

This ratio of the dimensions of the crystallographic element the author terms the "topical" axial ratio (*τόπος*, space); for a crystalline system of lower symmetry than the tetragonal, the topical axial ratio contains three terms,  $\chi : \phi : \omega$ , representing the dimensions of the elementary parallel-pipedon in the three crystallographic directions  $a$ ,  $b$ , and  $c$ . The topical axial ratio consequently measures the distances between the elements of crystalline structure in the three directions  $a$ ,  $b$ , and  $c$ .

The author has calculated the topical axial ratios for the tetragonal ammonium and potassium arsenates and phosphates as follows.

	$\phi$ .	:	$\chi$ .	:	$\omega$ .
$\text{KH}_2\text{PO}_4$ .....	3.1419	:	4.4432	:	2.9503
$\text{KH}_2\text{AsO}_4$ .....	3.2232	:	4.5583	:	3.0235
$\text{NH}_4\text{H}_2\text{PO}_4$ .....	3.1698	:	4.4827	:	3.1934
$\text{NH}_4\text{H}_2\text{AsO}_4$ .....	3.2491	:	4.5949	:	3.2606

For purposes of comparison,  $\chi$  is calculated as the diagonal of the square of side  $\phi$ ; consequently  $\chi = \phi\sqrt{2}$ . By comparison and subtraction of these numbers it is seen (1) That the distances of the molecules from each other in ammonium or potassium phosphate are increased by the same ratio in each direction when arsenic is substituted for the phosphorus; (2) That the increase in this distance is approximately the same in both ammonium and potassium salts; (3) That

on substituting arsenic for phosphorus in potassium or ammonium phosphate, the centres of gravity of the crystal molecules move further apart and to an equal extent in all directions; (4) That on replacing potassium by ammonium in potassium phosphate or arsenate, the distances between the centres of gravity of the molecules become greater, the maximum increase occurring in the direction of the principal axis  $c$ , and the minimum in the direction of the secondary axis  $a$ . From these conclusions, the author deduces that the crystalline molecules of these phosphates consist of eight chemical molecules.

The author has obtained most perfect crystals of the orthorhombic permanganates of the alkali metals by allowing hot concentrated solutions of the salts to cool in a water-jacketed vessel containing 25 litres of hot water; the cooling occupied five days. The following results were obtained.

Salt.	$a : b : c$	$x : \phi : w$	Sp. gr. at 9–10°.
KMnO <sub>4</sub> ...	0·79724 : 1 : 0·64908	3·8554 : 4·836 : 3·139	2·7035
NH <sub>4</sub> MnO <sub>4</sub> ..	0·8164 : 1 : 0·6584	3·9767 : 4·8711 : 3·2071	2·2076
RbMnO <sub>4</sub> ...	0·83110 : 1 : 0·66616	4·0322 : 4·8517 : 3·2312	3·2248
CsMnO <sub>4</sub> ...	0·86831 : 1 : 0·68525	4·2555 : 4·9009 : 3·3584	3·5974

The molecular volumes of the four salts are 58·526, 62·126, 63·228, and 70·042 respectively.

The relations observed by Tutton (Trans., 1893, 337) between the crystalline forms of the double sulphates containing potassium, rubidium, and caesium, are found still to hold between those of the permanganates. The differences between the axial ratios of the potassium and rubidium salts are the same as between those of the rubidium and caesium salts. The difference between the molecular volumes of caesium and rubidium permanganates is greater than the corresponding difference for the potassium and rubidium salts; this, the author shows, is always true for isomorphous salts of these three metals. The author concludes, further, that in an isomorphous series an increase in molecular weight is accompanied by an increase in molecular volume, if the elements which differ in the various members belong to the same group in the periodic system; if the latter is not the case, no relation is found between the molecular volumes and the molecular weights.

Very similar conclusions are drawn from the topical axial ratios of the permanganates as are deduced above from the phosphates and arsenates. The topical axial ratio of potassium perchlorate is also considered in its relation to that of the permanganate, and a comparison of Bravais' space lattice theory and Sohncke's point system theory of crystalline structure is made.

W. J. P.

**System of the Haloid Salts according to the Theory of Chemical Forms.** By F. FLAVITZKY (*J. Russ. Chem. Soc.*, 25,

223—262).—The author, feeling the insufficiency of the ordinary theory of valency to account for many types of the inorganic compounds, has developed a theory of chemical forms which is intended to embrace not only the common anhydrous compounds, but also the hydrated acids, salts, &c. To take an example, the forms derived from the theory for the elements of the seventh periodic group are as follows.

Fundamental forms— $R(OH)_7$ ,  $RH(OH)_6$ ,  $RH_2(OH)_5$ ,  $RH_3(OH)_4$ ,  $RH_4(OH)_3$ ,  $RH_5(OH)_2$ ,  $RH_6$ .

From these are derived the primary anhydrides.

- (a.) Saturated,  $R(OH)_7O$ ,  $RH(OH)_6O$ ,  $RH_2(OH)_5O$ ,  $RH_3(OH)_4O$ ,  $RH_4(OH)_3O$ ,  $RH_5O$ .  
 (b.) Unsaturated,  $[R(OH)_6]''$ ,  $[RH(OH)_5]''$ ,  $[RH_2(OH)_4]''$ ,  $[RH_3(OH)_3]''$ ,  $[RH_4(OH)_2]''$ ,  $[RH_5(OH)]''$ ,  $[RH_6]''$ .

The secondary anhydrides are

- (a.)  $R(OH)_6O_2$ ,  $RH(OH)_5O_2$ ,  $RH_2(OH)_4O_2$ ,  $RH_3O_2$ .  
 (b.)  $[R(OH)_5O]''$ ,  $[RH(OH)_4O]''$ ,  $[RH_2(OH)_3O]''$ ,  $[RH_3O]''$ .  
 (c.)  $[R(OH)_4]^{iv}$ ,  $[RH(OH)_3]^{iv}$ ,  $[RH_2(OH)_2]^{iv}$ ,  $[RH_3]^{iv}$ .

The tertiary anhydrides are

- (a.)  $R(OH)_5O_3$ ,  $RHO_3$ .  
 (b.)  $[R(OH)_4O]''$ ,  $[RHO_2]''$ .  
 (c.)  $[R(OH)_3O]^{iv}$ ,  $[RHO]^{iv}$ .  
 (d.)  $[R(OH)]^{vi}$ ,  $[RH]^{vi}$ .

In this paper, the author discusses the haloid salts, and refers them to the various forms given above; thus the salt  $LiClO_4 \cdot 3H_2O = Cl(LiH_3)O$ , corresponds with the first of the fundamental forms, the acid  $HClO_4 \cdot 2H_2O = Cl(OH)_6O$  to the first of the primary saturated anhydrides, the salt  $LiI \cdot 3H_2O = I(LiH_3)(OH)$ , to the fifth of the fundamental forms, the salt  $NaI \cdot 2H_2O = I(NaH_3)(OH)O$  to the fifth of the primary saturated anhydrides, &c. J. W.

**Stereochemistry.** By SEELIG (*J. pr. Chem.*, [2], 49, 134—136).—Remarks on the utility of stereochemical theories. A. G. B.

**Decomposition of Solutions by Contact with finely subdivided Silica, Titanic acid, Stannic Oxide, Alumina, Ferric Oxide, Magnesium Carbonate, Calcium Carbonate, or Barium Sulphate.** By G. GORE (*Chem. News*, 69, 22—24, 33, 43—46).—To ascertain the effect produced by silica, various solutions of known composition and strength were shaken, in quantities of 25 c.c., with 50 grains of suitably prepared pure precipitated silica, and allowed to settle during 16 to 20 hours; the supernatant liquids being then analysed. The following solutions lost in strength:—*Solutions of less than 1 per cent.*, hydrochloric acid, potassium and sodium chlorides, carbonates and cyanides, ammonium carbonate and iodine; *1, 5, and 10 per cent. solutions of* hydrochloric acid, zinc, magnesium, calcium and ammonium chlorides, potassium and sodium carbonates

and cyanides, ammonium hydroxide and carbonate, and potassium bromide; 5 and 10 per cent. solutions of nitric acid, potassium iodide and sodium bromide; 1 and 10 per cent. cadmium, strontium, and sodium chlorides, and potassium hydrogen sulphate; 1 and 5 per cent. potassium chloride. 10 per cent. solutions, acids—hydrobromic, hydriodic, chloric, perchloric, iodic, phosphoric, pyrophosphoric, tartaric and citric; chlorides—cobalt, barium, lithium, rubidium; sulphates—copper, iron, ammonium and rubidium; potassium nitrate, sodium and rubidium iodides, ammonium bromide, and trimethylamine; 5 per cent. succinic acid and disodium hydrogen phosphate. The following solutions gained in strength:—1 per cent. pyrophosphoric acid, 1 and 10 per cent. copper chloride, 10 per cent. cobalt, manganese, cadmium, zinc magnesium, sodium and potassium sulphates, and manganese chloride; and 5 per cent. potassium chlorate and iodate. The following solutions were apparently unaffected:—1 and 10 per cent. sulphuric acid; 1 and 5 per cent. lithium chloride, sodium iodide, and ammonium bromide; 10 per cent. chromic acid, nickel chloride and sulphate, potassium chloride and hydrogen sulphate, iron chloride, and rubidium bromide; 5 per cent. oxalic acid, cadmium, strontium and sodium chlorides, and potassium nitrate; 1 per cent. nitric, perchloric and phosphoric acids, zinc sulphate, potassium iodide and sodium bromide, 3 per cent. borax and  $\frac{1}{10}$  per cent. potassium, and  $\frac{1}{10}$  per cent. sodium chloride.

Increasing the amount of silica also increases the effect; the character of the solvent alters the effect, which, however, is not much changed by variations in temperature. Shaking with, is found more effective than percolation through, silica. The action is complete within four hours, and with acid and neutral salts, as is shown, is not regular; but with alkaline salts the amount abstracted from solution is generally greater, but the proportion less, the stronger the solution. Salts in admixture interfere with one another. With pulverised titanate acid, 1 per cent. potassium, sodium, and ammonium carbonates, and ammonium hydroxide lost in strength, but to a less extent than with silica; 1 per cent. potassium cyanide was not affected. Neither stannic oxide nor calcium carbonate was effective in four hours, whilst alumina, ferric oxide, magnesium carbonate, and barium sulphate were less active than silica. Barium sulphate formed in the solution was found more active than the previously prepared precipitate. Mixed powders, such as silica and alumina, silica and barium sulphate, like the mixed salts, interfere with one another's action. The wetting of the powder is in all cases accompanied by an evolution of air bubbles. The results show that the abstraction of dissolved substances from solution by finely-divided solids depends not only on the character and quality of the solid, but also on the strength and composition of the solution, and on the nature of the solvent employed.

D. A. L.

**A New Thermometer for High Temperatures.** By E. C. G. BALY and J. C. CHORLEY (*Ber.*, 27, 470—471).—The instrument is made like an ordinary thermometer, but of "resistance"-glass, which will stand a red-heat; it is filled with a liquid alloy of sodium and

potassium, and is graduated from 200 to 650°. The space above the alloy is filled with nitrogen at such a pressure that, when the bulb is red hot, and consequently somewhat soft, the pressure inside is equal to that of the atmosphere. Only the bulb and 9 cm. of the stem are exposed to the temperature to be measured, but no correction is needed, for the stem is graduated in equal divisions, whereas the coefficient of expansion of the alloy increases with the temperature. The glass of the bulb is attacked by the alloy and turned brown, but this occurs at the time of filling the bulb, and the coating then formed upon the surface of the glass protects the latter from subsequent action of the alloy.

C. F. B.

**Oven for the Prevention of the Explosion of Sealed Tubes.** By C. ULLMANN (*Ber.*, 27, 379—382).—In order to prevent, or in any case minimise, the risk of explosion of sealed tubes, the author introduces the sealed tubes into a strong steel tube, tested to 600 atmospheres, and containing 40—70 c.c. of ether, light petroleum, or other suitable liquid which does not attack glass at a high temperature. The steel tube is closed by means of a screwed cap and leaden washer, and heated as usual in a stove to the requisite temperature. The pressure caused by the vapour tension of the liquid in the steel tube more or less counteracts the pressure inside the glass tube, and thus reduces the risk of explosion to a minimum. In cases where the glass tube contains acid, pieces of lime are introduced into the steel tube to prevent corrosion of the latter in case of failure of the glass.

H. G. C.

## Inorganic Chemistry.

**Preparation of Hydrogen Peroxide.** By P. SHILOFF (*J. Russ. Chem. Soc.*, 25, 293—294).—Sodium carbonate is added to the commercial 3 per cent. aqueous solution of hydrogen peroxide, until the reaction is distinctly alkaline. The solution is then filtered, and shaken up for 3 to 5 minutes with 10—12 times its volume of ether, which extracts about half of the hydrogen peroxide originally present, and leaves behind most of the impurities. The ethereal layer is separated and reduced to 0.01—0.0025 of its original volume on the water bath. The remainder of the ether is removed in a bell-jar by solid paraffin. The loss of hydrogen peroxide during the evaporation of the ether is only 7—10 per cent.

Operating in this way, the author obtained (a) a colourless solution with distinctly acid reaction, and sp. gr. 1.1756, which contained 54 grams of anhydrous hydrogen peroxide in 100 c.c.; (b) a thick, transparent, slightly yellow, acid liquid, of sp. gr. 1.2475, which contained 79.6 grams of hydrogen peroxide in 100 c.c.

J. W.

**Source of Atmospheric Hydrogen Peroxide.** By A. BACH (*Ber.*, 27, 340—344).—The author has been led to the conclusion

that carbonic acid in sunlight undergoes decomposition into percarbonic acid and the elements of formaldehyde, according to the equation

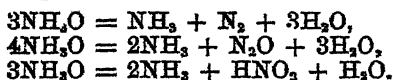


The percarbonic acid may afterwards decompose into carbonic anhydride and hydrogen peroxide,  $\text{H}_2\text{CO}_4 = \text{CO}_2 + \text{H}_2\text{O}_2$ . To these reactions, he attributes the presence of hydrogen peroxide in the atmosphere.

A cold, saturated, and filtered solution of uranium acetate, containing 1 per cent. of freshly-distilled diethylaniline, gives a violet coloration when exposed to the simultaneous action of carbonic anhydride and strong sunlight, although it is unaffected in this sense by either of these agents separately. This must be due to the formation of formaldehyde and of a compound (percarbonic acid), which will oxidise the leuco-base produced by the action of the formaldehyde on the diethylaniline.

J. W.

**Decomposition of Hydroxylamine by Sodium Hydroxide.** By S. KOLOTOFF (*J. Russ. Chem. Soc.*, 25, 295—296).—An aqueous solution containing 6 grams of hydroxylamine sulphate and 12 grams of sodium hydroxide in 90 c.c. was allowed to remain for several days at the ordinary temperature. It was then found that all the hydroxylamine had decomposed in the sense of the following equations



Hydroxylamine sulphate contains 17·07 per cent. of nitrogen, which was found to be distributed amongst the products of decomposition as follows.

Nitrogen in ammonia.....	7·12 per cent.
„ sodium nitrite.....	0·39 „
„ nitrous oxide.....	2·22 „
Free nitrogen.....	6·68 „
	<hr/>
	16·41 „

When hydroxylamine is oxidised by the calculated quantity of sodium hypobromite in alkaline solution, and by potassium permanganate in acid solution, hyponitrous acid is formed in small quantities, probably from the action of the nitrous acid primarily obtained on the excess of hydroxylamine.

J. W.

**Compounds of Hydroxylamine with Metallic Salts.** By W. FELDT (*Ber.*, 27, 401—406).—The following compounds have been prepared.  $\text{CoCl}_2 \cdot 2\text{NH}_2\text{O}$  is obtained by heating cobalt chloride with hydroxylamine hydrochloride and a little free hydroxylamine in alcoholic solution, on the water bath, in an atmosphere of hydrogen. It forms pink crystals, which decompose in the air, more rapidly when exposed to light, with formation of nitrous acid, but may be



preserved in closed vessels; when heated, it decomposes suddenly, with formation of vapours of ammonia and ammonium chloride.

$\text{CoSO}_4 \cdot \text{NH}_3\text{O} + 2\text{H}_2\text{O}$  is prepared in a similar manner, aqueous solutions being, however, employed. It is insoluble in cold water, but dissolves in hot water; oxidation, accompanied by the separation of a brown product, however, soon occurs in the solution. The salt is more stable than the chloride, and may be preserved for some time in the air.

$\text{CoOCl}_2 \cdot 2\text{NH}_3\text{O}$  is an unstable insoluble substance, obtained by passing oxygen, under an extra pressure of  $\frac{1}{4}$  atmosphere, into an alcoholic solution of cobalt chloride and free hydroxylamine. When this compound is suspended in cooled alcohol and treated with alcoholic hydrochloric acid, the salt,  $\text{CoCl}_2 \cdot 6\text{NH}_3\text{O}$ , is formed as a yellow, crystalline precipitate; the latter dissolves in acidified water, crystallises in the monosymmetric system, and is dissolved without decomposition by concentrated sulphuric acid; it corresponds in composition with luteocobalt chloride. When ammonium oxalate is added to its aqueous solution, a precipitate, consisting of yellow needles of the composition  $\text{Co}_2(\text{C}_2\text{O}_4)_3 \cdot 12\text{NH}_3\text{O}$ , is formed.

$\text{MnCl}_2 \cdot 2\text{NH}_3\text{O}$  is a very stable substance, and only decomposes at  $150-160^\circ$ .  $\text{MnSO}_4 \cdot \text{NH}_3\text{O} + 2\text{H}_2\text{O}$  is a white powder, insoluble in water. Attempts to obtain additive products with salts of copper and mercury proved unsuccessful.

A. H.

**Diamidophosphoric acid and Diamidotrihydroxyphosphoric acid.** By H. N. STOKES (*Ber.*, 27, 565—567).—*Diamido-orthophosphoric acid* is obtained in a similar manner to the monamido-acid (*Abstr.*, 1893, i, 316), by treating the dichloride of phenylphosphoric acid with aqueous ammonia, and hydrolysing the product. It is a crystalline substance, which is stable when dry, and is readily decomposed by acids, but is scarcely attacked by boiling aqueous alkalis. Nitrous acid converts it, first, into monamidophosphoric acid, and then into orthophosphoric acid itself. With the alkali metals and alkaline earth metals, it forms salts, which are remarkably soluble in water, and do not crystallise. The silver salt,  $\text{PO}(\text{NH}_2)_2 \cdot \text{OAg}$ , crystallises well; a second silver salt is also known, which has the composition  $\text{P}(\text{NH})(\text{NH}_2)(\text{OAg})_2$ , and is amorphous. When this substance is boiled with water or allowed to remain for two days under cold water, it is converted into the primary salt, and a splendid dark red salt, which probably has the composition  $\text{P}(\text{NAg})(\text{NHAg})(\text{OAg})_2$ , detonates slightly when heated, and is decomposed by concentrated sulphuric acid with production of flame.

When the first-mentioned salt is covered with aqueous potash of moderate concentration, it swells up, forming a stiff, colourless jelly, which, on dilution with water, yields a remarkably viscid solution; the jelly probably contains the salt  $\text{P}(\text{NH}_2)_2(\text{OK})_2 \cdot \text{OAg}$ . After some hours, colourless needles having the composition  $\text{P}(\text{NH}_2)_2(\text{OAg})_2 \cdot \text{OK}$ , are deposited from this jelly, whilst the mother liquor contains potassium diamidophosphate and free alkali. If these needles are washed with water, decomposition takes place, and a yellow-coloured substance of the formula  $\text{P}(\text{NH}_2)_2(\text{OAg})_2$  is free

formed, which again, on treatment with hot water, is converted into free acid, and a reddish-brown substance containing 4 atoms of silver,  $P(NHAg)_2(OAg)_2OH$ ; this is finally converted into the red salt, described above, by boiling with water.

If the viscid solution, already referred to, be further diluted with water, a clear, wine-red solution is obtained, from which carbonic anhydride precipitates an amorphous substance, which in appearance resembles freshly precipitated ferric hydroxide, and has the composition  $P(NHAg)_2(OAg)_2OH$  (see above). It explodes feebly when heated, and on boiling with water is converted, with loss of the elements of water, into the red salt.

If the jelly is so far diluted with water that it only contains 2—3 per cent. of alkali, a brown, amorphous salt, resembling silver oxide, is deposited, which has the formula  $P(NHAg)_2(OAg)_2$ . In the dry state, it explodes violently when rubbed, heated, or brought into contact with concentrated sulphuric acid.

Diamidophosphoric acid appears, therefore, to be capable of combining with 1 mol. of water or base to form the diamide of a pentabasic phosphoric acid, in which the two amido-groups play the part of hydroxyl-groups, 1 atom of hydrogen in each being replaceable by metals.

A. H.

**An Application of Sodium Silicate.** By G. GEISENHEIMER (*Compt. rend.*, 118, 192—194).—In order to ensure the complete bleaching of linen, it is customary to increase the causticity of the ley, and to prolong the time of boiling, with the result that the fabric is often injured. The production of yellowish or brownish patches is usually attributed to impurities in the chemicals used, but is chiefly due to the presence in the water of calcium and magnesium salts, which are precipitated on the fabric, and act as mordants, fixing the yellowish colouring matter of the ley. This injurious effect can be prevented by adding to the water a mixture of sodium carbonate and silicate; this precipitates calcium and magnesium silicates in a flocculent form, which settles rapidly, does not adhere to the fabric, and becomes granular and pulverulent on boiling with water. Thus purified, only a very small quantity of caustic alkali is necessary, the greater part of the saponification being effected by means of the less injurious alkali carbonate.

A convenient form in which to use sodium silicate is to add from 10 to 20 per cent. of anhydrous sodium carbonate to a saturated solution of sodium silicate. The product is easily handled, and remains completely soluble in water. Further, the quantity necessary for a particular water can readily be calculated.

C. H. B.

**Reproduction of the Diamond.** By H. MOISSAN (*Compt. rend.*, 118, 320—326).—Attempts to employ bismuth, in place of iron or silver, in the preparation of carbon under high pressure (*Abstr.*, 1893, ii, 275) were unsuccessful, the fused mass exploding violently when plunged into water. Further experiments with iron have confirmed the previous results (*loc. cit.*), but the yield of diamonds of sp. gr. between 3.0 and 3.5 is extremely small. Experiments with larger

quantities of iron gave no better results, seemingly because of the difficulty of saturating the metal with carbon. In order to obtain more rapid cooling, the fused iron saturated with carbon was poured into a cavity in a mass of iron filings. In this way small, rounded diamonds were obtained, which rarely showed any crystalline appearance, and they almost always enclosed black specks. They have a sp. gr. of 3.5, scratch rubies, and burn readily in oxygen.

The molten iron cannot be cooled in tin, because of the readiness with which the two metals unite, but it can be cooled by pouring it into a bath of melted lead; small globules of the iron rise to the surface, and are cooled and solidified before they reach it. When these solidified globules are treated with acids in the usual way, the yield of diamonds is somewhat better, and they are very limpid, have no black enclosures, and some show distinct crystallisation. They also show, in many cases, parallel striae, and impressions of cubes similar to those observed on certain natural diamonds. Two of the specimens broke spontaneously some time after preparation. One of the crystals showed distinctly curved faces. Some of the diamonds show smooth and brilliant surfaces, whilst others have a granular surface, such as is frequently seen on natural diamonds. Some of the crystals were found by Bouchardat to be trapezohedrons with 12 faces. With convergent polarised light, some of the crystals showed no coloration, whilst others showed feeble colours, much less intense than the colours observed with many natural crystals under similar conditions. From the appearance of the crystals, it seems probable that carbon, like iodine and arsenic, changes at the ordinary pressure, and at a sufficiently high temperature, from the solid to the gaseous state, but under a very high pressure can be liquefied, and remain in superfusion, taking a crystalline form when it solidifies.

Further experiments with silver saturated with carbon gave results similar to those previously described (*loc. cit.*), but only black diamonds were obtained.

0.0155 gram of diamonds heavier than methylene iodide gave 0.0496 gram of carbonic anhydride and 0.0025 gram of ash.

C. H. B.

**Behaviour of the Liquid Alloy of Sodium and Potassium in Contact with Dry Oxygen Gas.** By G. S. JOHNSON (*Chem. News*, 69, 20).—The liquid alloy of sodium and potassium remains unaltered in dry oxygen gas at the ordinary temperature, but at a temperature below redness it kindles and burns with explosive violence.

D. A. L.

**Pentahydrates of Sodium Bromide and Sodium Iodide.** By I. PANFILOFF (*J. Russ. Chem. Soc.*, 25, 272—275).—The pentahydrate of sodium iodide is obtained by cooling a solution of sodium iodide (100 grams) in water (50 c.c.) to  $-14^{\circ}$ , the temperature rising to  $-13.5^{\circ}$  when the crystallisation begins. At  $-10^{\circ}$ , it passes into the dihydrate and water.

The pentahydrate of sodium bromide crystallises slowly from a strong aqueous solution at the out-door winter temperature in Russia. It decomposes into the dihydrate and water at  $-25^{\circ}$ .

J. W.

**Hydrogel and Crystalline Hydrate of Copper Oxide.** By J. M. VAN BENNELEN (*Zeit. anorg. Chem.*, 5, 466—483).—The colloidal hydrate (hydrogel) is purified by repeated and rapid washing with large quantities of cold water (1 litre per gram), the mass being collected on a cloth filter after each washing, and the operation not lasting more than an hour, to avoid change of colour. The pure hydrogel is a thick, bright blue jelly, which, after pressing between porous earthenware for two hours, still contains a large quantity (20 mols.) of "water of absorption." It retains its colour under water at the ordinary temperature for several days, whether in the dark or in sunlight, but in hot water, unlike the crystalline variety, undergoes gradual modification, the colour changing to green. When, exposed at the ordinary temperature to an artificially dried atmosphere, it loses water until its vapour pressure is equal to that of the aqueous vapour in the atmosphere, and when the pressure is zero, the composition approaches the limit  $\text{CuO}, \text{H}_2\text{O}$ . This last molecule of water is only partially eliminated at  $100^\circ$ ; the second, although not so tenaciously attached, is more firmly combined than the others, the number of which varies, as before stated, with the pressure. With the elimination of water, the compound becomes more stable, and like the crystalline hydrate in character, whilst the ease with which the water is eliminated diminishes as time elapses; alkalis, however, facilitate the elimination. The dried substance absorbs a certain amount (4 mols.) of the water again, when exposed to a moist atmosphere, the exact amount depending, as before, on the pressure of the aqueous vapour in the atmosphere. The hydrogel is stable towards alkalis and alkali salts, but precipitates bromides and iodides, almost completely, as basic cuprous compounds; the fresher the preparation, the more vigorous the action.

The crystalline hydrate,  $\text{CuO}, \text{H}_2\text{O}$ , prepared by the slow action of dilute alkalis on various copper salts in the cold, is not affected by alkalis or by heat, and may be boiled with water without undergoing any change. The assumption of this stable form is in some way connected with the action of the alkali, as the same phenomenon is observed with beryllia and alumina. J.N. W.

**Interaction of Ferric Chloride with Potassium and Hydrogen Iodides.** By K. SEUBERT and A. DORRER (*Zeit. anorg. Chem.*, 5, 411—436).—A continuation of previous work (Abstr., 1894, ii, 140). The action with hydrogen iodide closely resembles that with potassium iodide. With molecular proportions ( $\text{FeCl}_3 : \text{HI}$ ), the yield of iodine never approaches the theoretical, though it increases steadily with the time, from 38.2 per cent. in 15 minutes to a maximum of 73.2 per cent. in 58 days. With increasing proportions of hydrogen iodide, but the same concentration of ferric chloride, the yield also increases, reaching 95.4 per cent. in 15 minutes, and a maximum of 98.9 per cent. in 17 hours with the ratio  $\text{FeCl}_3 : 5\text{HI}$ , and 99.0 and 100.8 per cent. in 18 hours with the ratios  $\text{FeCl}_3 : 10\text{HI}$  and  $\text{FeCl}_3 : 15\text{HI}$  respectively. With the ratio  $10\text{FeCl}_3 : \text{HI}$ , and the same concentration of hydrogen iodide as in the first experiment, 73.2 per cent. of the theoretical amount of iodine is liberated in 15 minutes,

and 98 per cent. in 25 hours; with the ratios  $15\text{FeCl}_3:\text{HI}$  and  $20\text{FeCl}_3:\text{HI}$ , 97.8 and 100 per cent. respectively in 18 hours.

Continuing the experiments with potassium iodide, the yield diminishes with the concentration, and, finally, almost vanishes. Mixed in molecular proportion and at concentrations twice and four times that in the previous experiments, the yield, in about 42 hours, increases from 59.9 per cent. to 67.5 (70.3 in 143 hours) and 75.2 per cent., whilst at half the concentration it diminishes to 50.6, at one-fifth to 41.0, at one-thirtieth to 5.35, and at one-fortieth to 1.25 per cent. The effect of dilution on the influence of excess of either substance is to decrease the rate at which the yield attains the maximum, both with regard to time and to the ratios of the reacting masses.

The influence of temperature on the action is distinctly unfavourable, owing to the precipitation of ferric oxychloride, and consequent removal of iron from the sphere of action; this bye-action may, however, be eliminated by the addition of hydrochloric acid in the ratio  $\text{FeCl}_3:3\text{HCl}$ . The immediate yield (30 minutes) with the ratio  $\text{FeCl}_3:\text{KI}$  then increases from 39.9 to 79.5 per cent., but diminishes on keeping at the ordinary temperature, owing to the reabsorption of iodine, a limit being reached in 41 hours, practically identical with that attained by a similar unheated mixture, or by a mixture, in molecular proportion, of ferric chloride and hydrogen iodide of the same concentration. The same phenomenon occurs with other ratios of ferric chloride to potassium iodide.

It is thus evident that the action follows the course indicated by the usually accepted equation,  $\text{FeR}_3 + \text{MI} = \text{FeR}_2 + \text{MR} + \text{I}$ , only under very strictly defined and special conditions. This is to be accounted for on the hypothesis that the action is reversible in the sense expressed by the equation  $\text{FeR}_2 + \text{MR} + \text{I} = \text{FeR}_3 + \text{MI}$ , in which case the maximum or limiting yield in the foregoing experiments corresponds with the point of equilibrium at which the velocities of the opposing reactions are equal. That this supposition is correct is evident from the result of the interaction of various molecular proportions of iodine with a mixture of ferrous and potassium chlorides in molecular proportion; in every case, the amount of iodine remaining after 60 hours corresponds with that liberated by an equivalent mixture of ferric chloride and potassium iodide in the same time. It is only in extreme cases, therefore, that the amount of iodine corresponding with the first equation will be liberated. The reason that the full amount is liberated in the analytical processes of Topf (Abstr., 1887, 998) and Stortenbeker (Abstr., 1890, 1185) is that either the iron or the iodine is removed from the sphere of action, in the one case by the precipitation of basic ferric acetate, in the other by the distillation of hydrogen iodide.

As to the mechanism of the action, it is most improbable that the chlorine of the potassium chloride is displaced by free iodine, and another explanation must be looked for. It appears that a mixture of very dilute solutions of ferric chloride and potassium iodide exhibits, after a long time, a yellowish-brown colour, which is not destroyed by thiosulphate, and is much deeper than that of a solution of ferric chloride of corresponding strength. It seems to be due to ferric

chloriodide,  $\text{FeCl}_2\text{I}$ , a compound corresponding with Lenormand's chlorobromide,  $\text{FeCl}_2\text{Br}$  (Abstr., 1893, ii, 377), for a mixture of neutral aqueous ferrous chloride with alcoholic iodine exhibits also a brownish-red colour, which is likewise not due to free iodine. The substance is not ferric oxychloride,  $\text{FeCl}_2\cdot\text{OH}$ , for iodine is liberated on dilution with water, which could scarcely be the case if the oxychloride had been formed in accordance with the equation  $\text{FeCl}_2 + \text{I} + \text{H}_2\text{O} = \text{FeCl}_2\cdot\text{OH} + \text{HI}$ . The amount of iodine liberated corresponds, too, with that contained in the chloriodide. Attempts to obtain the compound in the solid state by evaporating the solvent yielded, however, only mixtures of its proximate constituents.

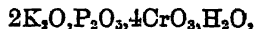
If this chloriodide, then, is formed as an intermediate product, the mechanism of the whole action is clear. The chloriodide is first produced in accordance with the equation  $\text{FeCl}_2 + \text{KI} = \text{FeCl}_2\text{I} + \text{KCl}$ , and then decomposed, more or less completely, into ferrous chloride and free iodine, according to conditions of time, concentration, temperature, and mass. But, since the latter reaction is reversible, the chloriodide, and, probably, the chloride, are formed again until equilibrium is attained, the actual position of the point of equilibrium depending on the conditions.

There is thus no need to assume, with Carnegie (Abstr., 1889, 1113), that potassium iodide is a direct reducing agent, nor, if means be taken to remove one of the products from the sphere of action, to require more than 1 mol. of potassium iodide for each mol. of ferric chloride. Duflos' equation,  $\text{FeCl}_3 + 3\text{KI} = \text{FeI}_2 + 3\text{KCl} + \text{I}$ , cannot, in any case, be true, for under the least favourable conditions of mass, 60 per cent. of the iodine in the potassium iodide is liberated.

JN. W.

**Phosphochromates.** By M. BLONDEL (*Compt. rend.*, 118, 194—195).

—When a highly concentrated solution of phosphoric and chromic acids, containing 8 mols. of the latter to 1 mol. of the former, is mixed with three-fourths of a molecular proportion of potassium carbonate, the salt,  $3\text{K}_2\text{O}, \text{P}_2\text{O}_5, 8\text{CrO}_3$ , is precipitated in the form of small, short prisms. If the solution contains only 2 mols. of chromic acid, the product is  $2\text{K}_2\text{O}, \text{P}_2\text{O}_5, 4\text{CrO}_3, \text{H}_2\text{O}$ , which crystallises in needles. If the latter solution, however, is mixed with some crystals of the first salt, the precipitate at first consists of this salt, which, however, if left in contact with the liquid, is converted into the second salt. The salt,  $3\text{K}_2\text{O}, \text{P}_2\text{O}_5, 8\text{CrO}_3$ , is converted into the salt



by treatment with water or a saturated solution of potassium dichromate.

C. H. B.

**Phosphovanadic Acids and their Salts.** By C. FRIEDHEIM (*Zeit. anorg. Chem.*, 5, 437—465; compare Abstr., 1890, 1067).—Although the vanadates are usually regarded as strictly analogous to the phosphates, they do not correspond with them in all respects. They show, for instance, a much greater tendency to form acid salts. When sodium metaphosphate and vanadate are brought together in

solution, the phosphate is converted into trisodium orthophosphate, whilst the vanadate assumes some such form as the acid salt,



or, if potassium chloride is present, an isomorphous mixture of potassium and sodium salts of a similar character. Monosodium orthophosphate behaves in much the same manner, and potassium pyrophosphate and pyrovanadate interact in a similar way.

On the other hand, it seems that the dark, reddish-brown *purpureo-salts* (*loc. cit.*), obtained from mixtures of monopotassium orthophosphate and potassium metavanadate, or of potassium metavanadate and phosphoric acid under certain somewhat indefinite conditions are isomorphous mixtures of monopotassium phosphate and vanadate. Although the salts obtained in this way in rectangular plates are somewhat variable in composition, the ratio of basic to acid oxide tends towards 1 : 2, and, in some cases, reaches that figure, whilst the ratio of phosphoric to vanadic acids approaches 1 : 12. They may thus be regarded as potassium divanadate,  $\text{K}_2\text{O}, 2\text{V}_2\text{O}_5$ , in which a portion of the vanadic oxide is isomorphously displaced by phosphoric oxide. Similar instances of isomorphous substitution of vanadium by phosphorus occur in the natural compounds *eusynchite* and *vanadinite*. Since, to form such isomorphous mixtures, potassium divanadate must be isomorphous with monopotassium orthophosphate, it would seem that the present nomenclature of the vanadates requires revision. It was incidentally observed that the *purpureo-salts* obtained by the addition of the proper amount of nitric acid to mixtures of potassium metavanadate and dipotassium orthophosphate were always contaminated with nitric acid, and it is possible that this may also exist in isomorphous replacement of vanadic acid, since nitrogen belongs to the same periodic group as vanadium and phosphorus.

The yellow, crystalline, *luteo-compound*,  $\text{K}_2\text{O}, \text{V}_2\text{O}_5, \text{P}_2\text{O}_5$  (*loc. cit.*), may be regarded either as having the constitution



with vanadoxyl functioning as base, or as an isomorphous mixture, similar in character to the *purpureo-compound*. The constancy and equality of the ratio of phosphoric to vanadic oxide is not out of harmony with the latter view, for similar compounds are known in *barytocalcite* and *zinc copper sulphate*. Another *luteo-compound* may be regarded as a mixture having the composition  $\text{PO}(\text{OK})_2 \cdot \text{O} \cdot \text{VO}_2 + \text{OH} \cdot \text{PO}(\text{OK}) \cdot \text{O} \cdot \text{VO}_2$ , analogous to sodium diphosphate. Others are still more complex.

When an excess of base is present in a mixture from which *purpureo-* or *luteo-compounds* might otherwise be expected, colourless, crystalline compounds separate, consisting of isomorphous mixtures of potassium metavanadate and monopotassium orthophosphate contaminated with dipotassium orthophosphate. JN. W.

## Mineralogical Chemistry.

**Analyses of the Mineral Combustible Gases of Torre and Salsomaggiore.** By D. GIBERTINI and A. PICCININI (*Gazzetta*, 23, ii, 559—576).—The authors have analysed a natural gas which issues at Torre in Parma; it is accompanied by water of alkaline reaction and a small proportion of petroleum. The gas contains about 95 per cent. by volume of methane and 0.12 per cent of carbonic oxide. A gas containing 91 per cent. of methane issues at Salsomaggiore, and is utilised as a source of heat and light. Full analyses are given.

W. J. P.

**Marly Limestones.** By H. LE CHATELIER (*Compt. rend.*, 118, 262—264).—Marls and marly limestones are generally regarded as intimate mixtures of calcium carbonate with clay. The author has previously shown that true clay consists of a mixture of quartz with an aluminium silicate,  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ , which is distinctly crystalline, loses water at about  $600^\circ$  if rapidly heated, and liberates heat suddenly at  $950^\circ$ . He finds, however, that the residues left after treating marly limestones with acetic acid never show the characteristic properties of true clays. They are richer in silica, although they contain no admixture of quartz; they lose their water at a lower temperature, show no sudden liberation of heat at a high temperature, and are sometimes amorphous, sometimes crystalline, but never show the crystalline form of true clay. The composition of the residue varies greatly with different marls;  $\text{SiO}_2$ , 51.6 to 66.1 per cent.;  $\text{Al}_2\text{O}_3$ , 16.1 to 21.2;  $\text{Fe}_2\text{O}_3$ , 3.6 to 7.2;  $\text{H}_2\text{O}$ , 9.0 to 19.5. The hydraulic limestone from the Congo leaves a residue which is distinctly crystalline, and has the composition  $2\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$ .

C. H. B.

**Occurrence of Diamonds in Meteorites.** By O. W. HUNLINGTON (*Proc. Amer. Acad.*, 29, 204—211).—In order to demonstrate that true diamonds occur in meteorites, the author dissolved many pounds of the Cañon Diablo iron in order to obtain enough diamond dust to use for cutting rough diamonds. About 200 lbs. of the iron was examined, and the most promising pieces were dissolved. About half a carat of diamond powder was finally obtained, being separated by its sp. gr. from a very large quantity of amorphous carbon.

The particles varied from colourless, through yellow and blue, to black. The diamond-cutting experiment was perfectly successful. The author's work establishes the fact that the Cañon Diablo iron contains true diamonds, and not any new allotropic form of carbon.

B. H. B.

**Analyses of German Mineral Springs.** By W. THÖRNER (*Ohem. Zeit.*, 17, 1411—1412).—The author gives the results of analyses of the water from (1) the Stahl spring, and (2) the Angelika spring at Tönnisstein, (3) the Wilhelms spring, and (4) the new spring at Melle, and (5) the sulphur spring at Lavern. The results were as follows, in grams per litre.



	1.	2.	3.	4.	5.
CaCO <sub>3</sub> .....	0·5285	0·4801	0·7373	1·1840	0·5632
MgCO <sub>3</sub> .....	0·8660	0·7819	0·3437	0·1470	0·0550
FeCO <sub>3</sub> .....	0·0162	0·0201	0·0149	0·1080	0·0001
Na <sub>2</sub> CO <sub>3</sub> .....	1·0214	0·8320	—	—	0·0968
NaCl.....	0·2819	0·1880	21·7117	17·6790	0·1286
KCl.....	0·0824	0·0741	0·0383	0·1290	—
LiCl.....	0·0146	0·0127	—	—	—
NH <sub>4</sub> Cl.....	0·0031	0·0041	—	—	—
Na <sub>2</sub> SO <sub>4</sub> .....	0·0927	0·0617	3·9121	3·1840	0·1330
RbCl.....	trace	trace	—	—	—
MgCl <sub>2</sub> .....	—	—	0·6788	0·0950	—
Al <sub>2</sub> O <sub>3</sub> .....	0·0132	0·0056	0·0679	0·0045	0·0020
SiO <sub>2</sub> .....	0·0312	0·0293	1·1150	0·0800	0·0230
Organic matter.....	0·0067	0·0075	0·0186	0·0112	0·0280
CO <sub>2</sub> .....	2·3844	1·9369	—	—	0·0610
CaSO <sub>4</sub> .....	—	—	1·2894	1·7780	0·1180
MgSO <sub>4</sub> .....	—	—	—	—	0·3480
K <sub>2</sub> SO <sub>4</sub> .....	—	—	—	—	0·0185
Na <sub>2</sub> S.....	—	—	—	—	0·0390
H <sub>2</sub> S.....	—	—	—	—	0·0187

B. H. B.

## Physiological Chemistry.

**Changes of Substance in the Horse.** By F. LEHMANN, O. HAGEMANN, and N. ZUNTZ (*Landw. Jahrb.*, 23, 125—165; compare Abstr., 1689, 911; 1890, 1170).—The objection has been made to the authors' previous experiments that they were of too short duration for the accurate estimation of the changes of a whole day. The first experiments now described were made in a Pettenkofer apparatus, which consists of a large case, in which the horse is placed, provided with windows and with pipes, &c., so that the air may be withdrawn and renewed as required. These experiments lasted over 24 hours. The daily weight of the horse, the amount and composition of food and excrement were determined, as well as the amount of carbonic anhydride of the respiratory gases before and after ignition. Other experiments were made, in which the earlier method (obtaining the gases directly from the trachea) and the Pettenkofer method were combined; these experiments lasted each about 10 hours. It was thus hoped to obtain trustworthy data as to the composition of the gases given off through the skin and intestines, inasmuch as the Pettenkofer method gives the total gases, and the trachea method the gases from the lungs alone. Earlier experiments on the skin respiration, as well as those made by Gerlach, seemed to indicate that the amount of carbonic anhydride so lost was very small, hardly more than 1 per cent. of that given off by the lungs.

The authors expressed the opinion in their former paper that the greater part (about three-quarters) of the intestinal gases were secreted through the lungs; this view, which was founded on Tacke's results ("Bedeutung der brennbaren Gase im thierischen Organismus," *Inaug. Diss., Berlin*, 1884), is now shown to be erroneous, as far as horses are concerned. Tacke's results, the correctness of which is not doubted, were made with rabbits, and cannot be applied to horses.

As regards the composition of the intestinal gases of horses, several samples of gas were directly collected for analysis. The collection of samples had to be done with great care, to avoid the admixture of air, as it was found that the pressure in the rectum is less than that of the atmosphere. The average percentage composition of four samples of intestinal gas was as follows.

CO <sub>2</sub>	CH <sub>4</sub>	H <sub>2</sub>	N <sub>2</sub>
22.49	59.92	2.59	15.00

Four more samples were taken from an old horse which had been fed for a week with oats (8 kilos.), hay (2 kilos.), and chaff (0.5 kilo. per day); the average composition was—

CO <sub>2</sub>	CH <sub>4</sub>	H <sub>2</sub>	N <sub>2</sub>
21.91	53.17	2.35	22.56

The horse was then killed, and samples of gas immediately taken from the cæcum and the colon. The composition of the gases was—

	CO <sub>2</sub>	CH <sub>4</sub>	H <sub>2</sub>	N <sub>2</sub>
From cæcum ....	78.70	5.29	0.89	15.12
From colon .....	72.74	17.28	0.84	9.14

In order to obtain evidence as to the nature of the gases evolved during fermentation after the horse was killed, weighed amounts of (1) the cæcum, (2) the colon, and (3) a mixture of fresh fæces with water were fermented, and the gases collected. The percentage composition was as follows.

	CO <sub>2</sub>	CH <sub>4</sub>	H <sub>2</sub>	N <sub>2</sub>
1. ....	95.96	0.75	2.91	0.38
2. ....	93.3	3.1	2.4	1.3
3. ....	58.47	0.89	36.96	3.68

The results obtained with gases collected immediately after the horse was killed, but especially these last results, differ considerably from those obtained by Tappeiner (*Abstr.*, 1882, 240), which made it seem probable that the fermentation remained unchanged for some time after death. The present results show a distinct change in the character of the fermentation after death, the marsh gas almost disappearing (compare Ellenberger, *Physiol.*, 1, 808; Lungwitz, *Arch. wissens. u. prakt. Thierheilkunde*, 18, 87; and Schierbeck, *Arch. Hygiene*, 16, 203).

The following conclusions are drawn from the results of the experiments. The gases exuded by horses contain, besides carbonic an-

hydride, some methane, the amount of which is, however, considerably less than that produced by ruminants. The average daily amount of methane was 21.0 grams. Hydrogen was found (in these experiments) in only small quantities, not more than 1 gram per day. Most of the methane is secreted from the rectum, accompanied with about 37.5 per cent. of its volume of carbonic anhydride. Apart from the carbonic anhydride from the lungs, the horse lost daily 73.9 litres, of which 60.6 litres passed through the skin, 13.3 litres through the rectum. The skin respiration amounts to about 2.5 per cent. of the lung respiration. In the measurement of the lung respiration alone, there is an error of about -3 per cent. When this is taken into account, the results obtained in the experiments of short duration agree with the 24-hour experiments obtained with Pettenkofer's apparatus. As regards the practical management of horses, there is much evidence of the effect of disturbances in the change of substance. Thus, the irritation caused by the presence of a few flies in the apparatus caused an increase in the production of carbonic anhydride amounting to over 10 per cent. of the total formed by a resting horse.

N. H. M.

**Effect on the Offspring of Calcium Phosphate, consumed during the Period of Gestation.** By L. GRAFFENBERGER (*Jour. f. Landw.*, 41, 57—61).—The results of Weiske's experiments (*ibid.*, 1888, 289) on the effect of calcium phosphate on the weight and composition of young rabbits showed an increase in amount of bone, free from fat, but there was no alteration in composition, and, in other respects, phosphate was without effect. According to Lehmann (*Ann. Chem. Pharm.*, 108, 357) and v. Gohren (*Landw. Versuchs-Stat.*, 3, 161), calcium phosphate is digested and assimilated by animals; Hoppe-Seyler (*Med. Chem. Untersuch.*, Heft 11) showed that, when mixed with human food, the salt is eliminated in the urine.

In the experiments now described, a litter of four rabbits, a week old, were killed with chloroform and analysed; the mother rabbit was then fed as before, but with addition of calcium phosphate (some grams per day), until a week after the birth of the next litter. The five young rabbits were then killed and analysed. Total weight, with and without skins, dry matter, fat, ash, lime, and phosphoric acid were determined. The results show that the calcium phosphate was without beneficial effect. The percentages of ash, lime, and phosphoric acid were somewhat diminished.

N. H. M.

**Substitution of Strontium for Calcium in the Animal Organism.** By H. WEISKE (*Landw. Jahrb.*, 23, 119—123).—A reply to the portion of Haselhoff's paper (this vol., ii, 207) dealing with the animal organism. The author maintains that, whilst strontium is not a poison, animals fed with it, instead of with calcium, will not live, and that whilst strontium may be conveyed to the flesh and bones, &c., it is not a substitute, physiologically, for calcium (compare Cremer, *Sitzungsber. d. Ges. Morph. Physiol.*, München, 7, 124).

N. H. M.

**Excretion of Sulphur.** By W. J. SMITH (*Pflüger's Archiv*, 55, 542—549).—In some sulphur-containing organic substances, the union of sulphur with carbon is so strong that the chemical decompositions accomplished in the body are unable to sever them. Such substances, of which acetone-ethylmercaptol and thiophen may be taken as instances, cause no increase in the sulphuric acid of the urine. The present experiments on a dog show that ethylic sulphide may be added to this list. The form in which the sulphur leaves the body was not, however, determined. These three substances have this in common, that the sulphur is combined thus,  $\text{C}\cdot\text{S}\cdot\text{C}$ . Nevertheless, there are substances, such as carbamino-thioglycolic acid, containing the same combination of their sulphur which do give rise to an increase of urinary sulphates. W. D. H.

**Human Pancreatic Ferments in Disease.** By V. D. HARRIS and C. A. CRACE-CALVERT (*St. Barth. Hosp. Rep.*, 29, 125—142).—23 pancreases were examined, removed at varying periods after death from various diseases, and compared with the normal pancreas from a case of accident. The methods were those previously adopted by one of the authors (*Abstr.*, 1893, ii, 22).

The number of cases is too small for general conclusions to be drawn. But the strength of the ferments was diminished in all cases, and markedly so in some. In a few cases, in children, it was impossible to show the presence of any ferments. The fat-splitting ferment was absent in about half the cases, the milk-curdling ferment in about half; the diastatic ferment was markedly diminished in brain cases, and to a less extent in all cases. The proteolytic ferment was the one least affected. It was, however, absent or feeble in cases of pneumonia, malignant disease, diabetes, and renal disease.

W. D. H.

**Albuminous Periostitis.** By L. HUGOUNENQ (*Compt. rend.*, 118, 149—150).—This rare disease is characterised by the accumulation under the periosteum of a liquid something like synovia. The liquid has a sp. gr. of 1.020 to 1.035, coagulates on heating to  $80^{\circ}$ , and contains a nucleo-albumin and an albumin resembling serum albumin. It frequently has fat droplets in suspension.

Quantitative analysis gave the following results.

Total solids .....	8.39 per cent.
Nucleo-albumin .....	0.87 "
Albumin .....	5.61 "
Succinic acid, urea, fat, and other extractives .....	0.98 "
Ash .....	0.93 "
Containing—	
Sodium chloride .....	0.43 per cent.
„ sulphate .....	0.04
„ phosphate .....	0.06
„ carbonate .....	0.22
Potassium chloride .....	0.08
Calcium phosphate .....	0.05

W. D. H.

**Action of Selenium and Tellurium on the Animal Organism.** By F. CZAPEK and J. WEIL (*Chem. Centr.*, 1893, ii, 1098; from *Arch. exp. Path. Pharm.*, **32**, 438—455).—No direct toxic action of selenium compounds could be demonstrated on cells; but they act poisonously on the animal body as a whole, and selenites more so than selenates. The metal is not poisonous. It is probable that selenates are reduced to selenites in the body. Here there is an analogy to arsenic and its compounds. The chief difference between selenium and tellurium is in the way it leaves the body. Tellurium is more rapidly reduced to the metallic state, which is harmless. Both elements, like arsenic, act by weakening the heart, lowering blood pressure, and paralysing the central nervous system. Antimony acts in a similar way.

W. D. H.

## Chemistry of Vegetable Physiology and Agriculture.

**Sulphydric Fermentation in the Black Sea.** By N. ZELINSKY (*J. Russ. Chem. Soc.*, **25**, 298—303).—The author has investigated samples of the ooze from the bottom of the Black Sea at depths of 16, 40, 389, 870, and 1207 fathoms, and from those dredged at the greater depths has succeeded in isolating various micro-organisms which possess the power of evolving hydrogen sulphide from the nutritive media in which they are cultivated. Amongst these there is one characterised by its great power of evolving hydrogen sulphide as well as by giving rise to a coffee-coloured pigment changing to black, when the microbe is cultivated in agar-agar. This microbe, which is a mobile, somewhat elongated bacterium, can live either in the presence or absence of atmospheric oxygen, and has been called by the author *Bacterium hydrosulfureum ponticum*.

The bacterium can evolve hydrogen sulphide not only from liquids containing proteid matter, but also from media in which the sulphur is present as a component of an inorganic salt. Thus hydrogen sulphide is soon detected in liquids in which the sulphur has been added in the form of sulphates, sulphites, thiosulphates, or even ammonium thiodiglycollate. In the estuary at Odessa, a microbe (*Vibrio hydrosulfureus*), described by Brusilovsky, is active in the same way, reducing salts containing sulphur and oxygen to hydrogen sulphide. The other important product of fermentation is ammonia.

J. W.

**Assimilation of Atmospheric Nitrogen by Microbes.** By S. WINOGRADSKY (*Compt. rend.*, **118**, 353—355).—The following table gives the results of three series of experiments with cultures of the three bacilli previously described (*Abstr.*, 1893, ii, 482—483). The nitrogen added to the cultures at the outset was in the form of ammonium sulphate.

1	{ Glucose in grams .....	20	40	20	20	100	200
	{ Nitrogen in milligrams { initial....	00	00	00	00	21	21
	{ increase..	58	97	39	49	157	244
2	{ Glucose in grams .....	1.0	2.0	30	40		
	{ Nitrogen in milligrams { initial....	106	106	106	106		
	{ increase..	0.0	08	37	4.1		
3	{ Glucose in grams .....	3.0	3.0	30	30	30	30
	{ Nitrogen in milligrams { initial....	21	4.2	6.4	8.5	17.0	21.2
	{ increase..	7.0	5.0	5.5	3.6	0.3	-2.2

It would seem that in media containing at the outset not more than traces of nitrogen, the quantity of nitrogen fixed is proportional to the quantity of glucose decomposed, but this ratio only holds good under strictly similar conditions. When nitrogen is present in the culture medium, the gain in nitrogen becomes much less regular, and a somewhat high proportion of glucose is necessary before any nitrogen is fixed at all. Further, even in presence of a high proportion of glucose, there is no gain in nitrogen if the initial proportion of this element exceeds a certain amount. The gain in nitrogen depends on the relation between the initial quantity of combined nitrogen and the initial quantity of glucose, and this ratio must be below 6:1000.

The bacillus which was regarded as the chief agent in fixing nitrogen (*loc. cit.*) was isolated by means of anaerobic cultures on sections of carrot. When the pure bacillus is sown in the glucose culture fluid exposed to air in thin layers, it refuses to grow, and all the cultures remain sterile for an indefinite period; but if the two other bacilli (*loc. cit.*) or some *mucedines* are introduced, fermentation and the development of the specific bacillus begin at once. The anaerobic character of the bacillus is further shown by its power of fermenting glucose in absence of air provided a small quantity of ammoniacal nitrogen has been added.

In order to obtain the maximum absorption of nitrogen, the pure bacillus should be introduced into a thin layer of glucose solution containing no combined nitrogen, but in contact with an atmosphere of pure nitrogen. In two experiments under these conditions, with 20 grams of dextrose, the gain of nitrogen was 23.0 and 24.7 milligrams respectively.

The bacillus does not germinate in broth or in gelatin. The chief products of the fermentation of the glucose are butyric, acetic, and carbonic acids and hydrogen, the gas that is given off sometimes containing as much as 70 per cent. of the latter.

It would seem that the absorption of free nitrogen is due to contact between this gas and nascent hydrogen within the living protoplasm, with the result that ammonia is formed. C. H. B.

**Nitrogen Question.** By G. LIEBSCHER (*Journ. Landw.*, 41, 139—198).—The chief object of the author's experiments was to ascertain how far Hellriegel's discovery that the *Leguminosæ* can utilise elementary nitrogen affects the cultivation of soils, Hellriegel's own results with senadella having indicated that the power of nitrogen fixation was much diminished in the presence of combined nitrogen. Inasmuch as in this case fixation was shown to depend partly on the

manuring, it seemed not impossible that conditions might exist under which non-leguminous plants—mustard, for instance, which is extensively employed in green manuring—might also be found to have the power of assimilating free nitrogen.

In 1888, a series of pot experiments were made in which peas, oats, and buckwheat were grown in arable soil; peas and oats in humus sand and in poor sandy soil as well. In the case of the arable soil, there were also fallow experiments. The amounts of soil in each pot were—arable, 11,270; humus sand, 13,046; poor sand, 14,135 grams; containing 14.50, 11.17, and 7.12 grams of nitrogen respectively (or 0.1287, 0.0856, and 0.0504 per cent.). Some pots had an application of nitrate, others horn-meal, and the rest no nitrogenous manure. As regards oats, the yield in the unmanured pots was greatest in the poor sandy soil (61.59 grams of dry substance), next in the humus sand (53.25 grams), whilst in the arable soil the yield was only 30.70 grams, owing to the greater stability of the nitrogenous matter. The yield was greatly increased by nitrate in the arable soil, only slightly in the humus sand, whilst in the poor sandy soil there was less growth under the influence of nitrate than in the unmanured pots. In every case (but especially in the arable soil), the produce was richer in nitrogen where nitrate or horn-meal had been applied; in the oats grown in arable soil, the percentage was raised from 0.76 to 1.10 and 1.36 by nitrate and horn-meal respectively. As regards peas, the greatest yield and the most nitrogenous produce was obtained in the arable soil; in the poor sandy soil, both the yield and the percentage of nitrogen of the produce were diminished by the application of the nitrogenous manure. The arable soil gained nitrogen in every experiment. In the fallow experiments, the gain was as follows:—Unmanured, 0.5669 gram; horn-meal pot, 0.4402 gram; nitrate pot, 0.2711 gram. It is assumed that there was a loss in each case (more than covered by the gain due to algæ), which is the greater the more soluble the nitrogenous matter present. Deducting the gains of total nitrogen of the fallow pots from the total gains of the vegetation pots, the following average results, due to vegetation alone are obtained.

	No nitrogenous manure.	Nitrate.	Organic nitrogen.
Peas .....	+0.7331	+0.8986	+0.9092
Buckwheat .	—	+0.6511	+0.4419
Oats .....	+0.2571	+0.6070	+0.1496

Peas, therefore, collected the greatest amount of nitrogen.

The experiments with the two sandy soils showed a loss of nitrogen in the soil in every case, and a loss of total nitrogen in nearly every case; the losses were less with oats than with peas. The results indicate that the final amounts of nitrogen are greatest where the growth was most luxuriant, with peas in presence of little available combined nitrogen, with oats in presence of the greatest amount of available combined nitrogen.

The next experiments (1891-92) were conducted in zinc cylinders, closed at the bottom to prevent loss by drainage, and holding about

17 kilos. of soil (1891) and 10·6 kilos. (1892); the soils contained 0·1404 and 0·1469 per cent. of nitrogen. In 1891, there were four fallow pots, six with oats, six with peas, and six with mustard; half of the pots had nitrate (0·9528 gram of nitrogen), the rest no nitrogenous manure, but the soil of each pot contained over 23 grams of nitrogen. The following average amounts of air-dried produce and nitrogen were obtained.

	No nitrate.		Nitrate.		Increase.	
	Produce.	N.	Produce.	N.	Produce.	N.
Oats.....	67·2	0·4614	98·6	1·2176	31·4	0·7562
Mustard.....	26·2	0·3584	54·6	1·3197	28·4	0·9613
Peas.....	60·5	1·1873	83·9	1·7552	23·4	0·5679

The percentage of nitrogen of the dry matter of the oats was raised from 0·6867 to 1·2344 under the influence of nitrate; in mustard from 1·3711 to 2·2973, whilst in peas there was no difference. The nitrogen applied was utilised to the extent of 59·6 per cent. by the peas, 79·4 per cent. by the oats, and 100·9 per cent. by the mustard. The soil lost nitrogen in every case, and it is assumed that there was no considerable gain by algae. As regards total nitrogen, the pea experiments nearly all show a gain, the others nearly all a loss. The following table shows the average gain or loss of nitrogen, and the effect of vegetation shown by the difference between the fallow and vegetation pots.

	Without nitrate.		With nitrate.	
	Gain or loss.	Effect of plants.	Gain or loss.	Effect of plants.
Fallow.....	-0·6878	—	-0·8517	—
Oats.....	-0·3145	+0·3733	-0·2236	+0·6231
Mustard.....	-0·0255	+0·6623	+0·0333	+0·8850
Peas.....	+0·6852	+1·3730	+0·3852	+1·2369

Nitrogen fixation is thus only proved in the case of peas, but the very considerable loss in the fallow pots (probably due to wetness and want of aëration) makes it probable that there was also fixation in the case of mustard.

In 1892, the experiments were—fallow, peas (both without nitrogenous manure, with mustard meal, and with nitrate), peas and mustard mixed (with and without nitrate), haricots (with and without nitrate), oats, oats and clover mixed, and mustard (all with nitrate). One of the fallow pots had also mustard oil. The object of sowing



mustard with clover, and of manuring with mustard meal, was to ascertain whether the presence of mustard had any injurious effect on the soil organisms and consequently on nitrogen fixation. By growing oats and clover together, it was thought possible that the abstraction of combined nitrogen by the oats might induce an increased assimilation by the leguminous plant. The fallow soils showed a gain of nitrogen with the exception of those which had mustard oil and mustard meal, which lost, probably owing to the injurious effect of mustard on the algæ. On the other hand, neither the mustard plants growing with the *Leguminosæ* nor the mustard meal had any effect on nodule production. In all the vegetation experiments there was a loss of soil nitrogen but a gain of total nitrogen. Owing to the presence of algæ in the fallow pots, no comparison can be made between pots with and without vegetation. As before, the peas collected nitrogen, and to a greater extent in absence than in presence of nitrate. Owing to the richness of the soil, the clover grown with oats did not fix nitrogen to any extent, as is shown by comparing the results with those obtained with oats alone. Oats with nitrate collected more nitrogen than peas with nitrate, whilst mustard collected on the average twice as much as the peas. Peas and mustard mixed fixed the greatest amount of nitrogen, especially in those pots to which nitrate was applied; in these pots the fixation was raised 70 per cent. over that of the unmanured pots. There is evidence that the excess of total nitrogen of the mustard and peas over that of the peas grown alone is due to the mustard and not to increased assimilation by the peas.

It is concluded, as established, that there is only a difference in degree between the nitrogen-fixing power of the leguminous and the non-leguminous plants; and it is probable that Frank's theory that all green plants assimilate free nitrogen is correct. The essential difference is that peas grow well and assimilate nitrogen when grown in soil poor in nitrogen, whilst in the case of non-leguminous plants, fixation is more or less dependent on the application of nitrogenous manure. This accounts for the negative results obtained with non-leguminous plants by Hellriegel and others, who employed sand free, or nearly so, from nitrogen, sometimes without and sometimes with very sparing addition of nitrate. Plenty of combined nitrogen must be given to these plants before they can assimilate free nitrogen, whilst *Leguminosæ* only require to be infected with nodule bacteria. As regards green manuring, a leguminous plant alone, mustard alone, or a mixture of the two, may be employed according to the conditions.

The method of analysis, which was carried out with great care, and the rather elaborate method of determining the error of analysis are given in detail. Large numbers of determinations were made in each case. As regards the experiments themselves, the most important error was the introduction of combined nitrogen by exposure to rain; it is thought, however, that this is not at all considerable, but it will be avoided in future experiments. No attempt was made to ascertain the part played by the soil algæ, as, at the time the experiments were made, the author was not aware of their importance. The gains found in the vegetation pots of 1892, as compared with the fallow pots, can, at

any rate, not be due to algæ. It is suggested as possible that the gain of nitrogen in the pots sown with mustard, &c., may have been due to the co-operation of micro-organisms, but further experiments will be required to decide this point.

N. H. M.

**Assimilation of Free Nitrogen by White and Black Mustard.** By J. P. LORSY (*Exper. Stat. Bul.*, No. 18, 1894).—White and black mustard were grown in pots in pure sand with minerals, and in water culture, both with and without nitrate. In the presence of combined nitrogen, the plants all grew well, and developed completely; but where no nitrate was given, the growth was slight, and the water culture plants died. The black mustard, however, which was grown without nitrate, developed more than the white mustard grown under the same conditions, indicating nitrogen-fixation. This may possibly be due to the vegetation of algæ.

Experiments made with the same plants, with and without nitrate under conditions of sterilisation, showed that whilst the nitrate plants grew well, those to which no combined nitrogen was given failed. Neither of the two species is, therefore, able to live in absence of combined nitrogen.

Sketches of the plants at different periods of growth, and of the apparatus, are given. No analyses are recorded.

N. H. M.

**Functions of Hops used in the Dry-Hopping of Beer.** By H. T. BROWN and G. H. MOREIS (*Trans. Inst. Brew.*, 6, 94—106).—The secondary fermentation which is brought about by adding a small quantity of hops to finished beer may be due to the occurrence in the hops of a fermentable sugar, an adherent "wild yeast," or an enzyme capable of hydrolysing the amyloins and dextrin of the beer. The phenomenon is found by the author to be mainly due to the last-named cause. The enzyme is present in greatest quantity in the hop strobiles, but also occurs in the leaves and seeds of the plant (compare also *Trans.*, 1893, 604). It was not isolated, for when the dried tissues are treated with a comparatively small quantity of water, sufficient tannin is extracted to prevent the enzyme passing into solution; when, however, a large quantity of water is used, the tannin forms such a dilute solution that it exerts little or no effect on the enzyme, which diffuses at a much slower rate.

A. R. L.

**Invertase in Bananas.** By F. MIERAN (*Ohem. Zeit.*, 17, 1283).—Ripe bananas contain invertase. An aqueous extract of the fruit made at ordinary temperatures, and afterwards digested at 55°, is lævogyrate  $[\alpha]_D = -7.15^\circ$ ; a similar extract made at 100° is dextrogyrate  $[\alpha]_D = +17.49^\circ$ . Cane sugar in solution is hydrolysed by treatment with the ripe fruit, in one instance the rotatory power  $[\alpha]_D = +99.6^\circ$  and  $-11.22^\circ$ , before and after the experiment respectively.

J. B. T.

**Chemical Properties of the Alcoholic Extract of Beer Yeast.** By J. DE REY-PAILHADE (*Compt. rend.*, 118, 201—203).—100 grams

of young pressed yeast containing 20 per cent. of dry matter is suspended in 55 grams of water containing a small quantity of glucose, and 45 grams of alcohol of 90° is added in successive small portions. A flask is filled completely with this mixture, stoppered, and allowed to remain at 0° with occasional agitation for three days. The contents are then filtered, and the filtrate passed through a d'Arsonval sterilising cylinder, and collected in a sterilised flask, which is made vacuous in order to remove the dissolved carbonic anhydride from the liquid.

The liquid thus obtained contains about 2.2 per cent. of alcohol, is slightly acid, and is free from living organisms. When brought in contact with sulphur, there is immediate formation of hydrogen sulphide; when heated at 45° in a sterilised and vacuous flask, carbonic anhydride is formed; when allowed to remain in contact with air, oxygen is absorbed, and carbonic anhydride is formed.

The alcoholic extract contains a considerable quantity of phloem, and attention is called to the similarity between the properties of this extract and those of extracts obtained from animal tissues.

C. H. B.

**Crystalloids of Protein.** By G. STOCK (*Ann. Agron.*, 20, 105—106; from *Ber. Sachs. Ges. Wiss. Math. Phys.*, 150, 638).—Acidified pepsin solution and a solution of pancreatin containing sodium carbonate both dissolve crystalloids of protein. The crystalloids disappear generally immediately before the death of leaves. Their production and solution does not seem to be affected by light. On growing plants in nutritive solutions, it was found that by withholding assimilable nitrogen, the crystalloids may be made to disappear, whilst the addition of nitrogen in a suitable form causes their reappearance. In presence of plenty of nitrogen, a diminution in the quantity of calcium causes a considerable accumulation of crystalloids. In the case of plants grown without lime, crystalloids appear in parts of the plants where they never occur under normal conditions. Crystalloids form in juices of leaves floated for some time on solutions rich in nitrogen.

N. H. M.

**Physiological Function of Calcium and Magnesium Salts in the Vegetable Organism.** By O. LOEW (*Ann. Agron.*, 20, 108—111; from *Flora*, 1892; *Bot. Centr.*, 51, 152).—Calcium is present in plants as a precipitant for oxalic acid, and also as a protoplasmic compound in the chlorophyll grains. This is why the greenest parts of the plant contain most of the calcium, and is also a reason why those plants which produce no oxalic acid still require lime.

Potassium oxalate is extremely poisonous towards green plants, and causes remarkable changes in the chloroplast, of, for instance, *Spirogyra majuscula*, and a whole series of other algæ. It has no effect on mushrooms. Potassium tartrate and sulphate have no appreciable effect. It is suggested that the oxalic present in plants liberates the lime from the protoplasmic compound causing the modified chlorophyll grains to swell—that was the effect observed

under the influence of potassium oxalate—and the albumen to pass from the active to the passive state. Oxalic acid itself is by far the most poisonous organic acid towards plants; a 0.004 per cent. solution causes the nucleus to swell, and to become opaque. It seems likely that calcium compounds have an important part in the nucleus, that a compound of calcium with nuclein forms the framework of the nucleus. If this is the case, the nuclei of lower fungi must be differently constituted, as oxalic acid has no effect on them. If it is admitted that such calcium compounds exist, the important effect of calcium in the transport of starch becomes more intelligible.

With regard to magnesium, the first question which arises is why it cannot be replaced by calcium. The reason is probably that magnesia is a very feeble base, and can be much more readily separated from acids than is the case with lime. This explains the injurious effect of magnesium salts when given alone to plants. Calcium salts when present prevent any injurious effect from magnesium salts, whilst sodium and potassium salts remain without effect; the magnesium salts then show their nutritive property, which depends on the ease with which they give up their acids, especially phosphoric acid. The tertiary phosphate of magnesium accumulates where the nuclein and lecithin are produced, and hence magnesia, like phosphoric acid, follows the proteids which accumulate in the seeds. This only holds good in the case of green plants. Just as in the case of lower vegetation, oxalates are not injurious, so also magnesium salts have no injurious effect on them in absence of lime.

N. H. M.

**Substitution of Strontium for Calcium as Plant Food.** By E. HASELHOFF (*Landw. Jahrb.*, 22, 851—861).—Hitherto experiments on the substitution of strontium for calcium have only been made with animal food. Papillon (*Compt. rend.*, 71, 372) showed that such a substitution may take place in bones. This was disputed by Weiske (*Zeit. Biol.*, 8, 239). J. König, however (*Landw. Jahrb.*, 3, 421), in experiments with rabbits came to the same conclusions as Papillon.

As regards plants, no experiments had as yet been made, although the question is one of some importance to agriculture, especially in Westphalia, where some soils contain considerable amounts of strontianite. The author grew barley and beans in a poor sandy soil, to which calcium and strontium carbonates respectively were added; he also grew beans and maize in nutritive solutions containing calcium and no strontium, and *vice versa*. The results show that strontium has no injurious action on plants; that it is taken up by plants, and seems to take the place of lime; and that it replaces lime only when the supply of lime and other substances are no longer adequate for the wants of the vegetable organism.

N. H. M.

**Ash Constituents of the Coffee Tree.** By F. W. DAFERT (*Landw. Jahrb.*, 23, 27—45).—The analyses were made in the Agricultural Institute of São Paulo, Brazil, the common coffee tree of the country being employed. The percentage results are given on p. 208.

It is noteworthy that the percentage of potash increases with the distance of the organ from the root, being highest in the leaves, and

that the lime is highest in the root, and diminishes with the distance from the root.

	Roots.	Stems.	Branches.	Leaves.	Husks.	Beans.
Pure ash in air dry substance .....	4.78	1.44	3.25	5.10	3.80	2.84
In pure ash—						
K <sub>2</sub> O .....	28.24	44.08	49.20	56.48	54.46	62.99
Na <sub>2</sub> O .....	3.28	1.92	0.58	1.43	2.08	—
CaO .....	18.99	18.99	33.03	21.65	10.20	5.18
MgO .....	8.58	9.35	7.62	6.57	4.35	11.45
Fe <sub>2</sub> O <sub>3</sub> .....	12.95	1.91	2.08	0.90	5.61	0.57
P <sub>2</sub> O <sub>5</sub> .....	4.21	4.49	4.52	6.07	4.44	14.16
SO <sub>3</sub> .....	4.61	2.10	1.94	3.51	2.98	5.05
SiO <sub>2</sub> .....	16.37	(0.45)	0.83	2.17	13.67	0.30
Cl. ....	1.63	(0.24)	0.61	0.51	0.60	0.33

N. H. M.

**Physiological Action of Tellurous Acid.** By T. BOKORNY (*Chem. Zeit.*, 17, 1598—1599).—The aqueous solution of this substance has no action on various algæ and infusoria. Its solubility in water is very small, and may be assisted by the addition of dipotassium phosphate. Under these circumstances, the solution is harmless to the organisms in question, and the histological appearances in cells, nuclei, chlorophyll granules, &c., are described as perfectly normal.

Selenious acid is more poisonous, and sulphurous acid more poisonous still.

W. D. H.

**Injurious Action of Nickel on Plants.** By E. HASELHOFF (*Landw. Jahrb.*, 22, 862—867).—Three soils from meadows which had been irrigated with contaminated waters, were found to contain copper oxide (0.63, 0.89, and 2.05 per cent.), zinc oxide (0.95, 0.83, and 0.60 per cent.), and nickel oxide (0.12, 0.20, and 0.15 per cent., reckoned in soil dried and free from humus). In order to ascertain the effect of nickel on plants, horse beans and maize were grown in nutritive solutions to which nickel sulphate was added in various amounts, containing from 2.5 to 50 milligrams of nickel oxide per litre. The smallest amount (2.5 milligrams per litre) was sufficient not only to stop growth but to kill the plants.

N. H. M.

**Composition of Algæ and other Marine Plants of the Coast of Algeria.** By J. A. MULLER (*Ann. Agron.*, 20, 82—91).—In the coast districts of Algeria, algæ are employed for manuring. They are first exposed to rain to wash out the salt, and dried in the sun, or else applied directly after they are sufficiently washed out. Sometimes after being washed by rain they are burnt, and the more or less carbonaceous ash used as manure. The plants examined by the author were collected at the Cape of Acrata, near Guyotville. Eleven species were examined, and the results of the nitrogen estimations and ash analyses

are tabulated in the original. The nitrogen varied from 0.75 to 1.83 per cent. of the dry matter in different species. N. H. M.

**Digestibility and Nutritive Value of various Grains.** By H. WEI-KE (*Landw. Versuchs-Stat.*, 43, 207—222).—It has already been shown that oats are digested by rabbits in varying amounts, being most thoroughly digested where small amounts were consumed (*Landw. Jahrb.*, 21, 791, and *Abstr.*, 1893, ii, 132). The experiments now described were made with sheep, which were first fed with 500 grams of air-dried oats daily. This experiment lasted for about a week, when they had to be discontinued as the sheep began to leave some of the food uneaten. During the experiment, the sheep took very little water; instead of about 2.5 parts of water to 1 of dry food, which is the usual amount, the consumption of water to dry food was only 1.2 and 0.8 : 1. The production of urine was very small, especially in the case of sheep No. 2 (average 40 c.c. daily); but the percentage of water in the fæces was high, especially towards the end of the experiment. Deducting the amounts of the various constituents of the fæces from those of the 500 grams of oats given daily, the following percentage amounts are found to be digested by the sheep 1 and 2.

	Dry matter.	Nitrogenous matter.	Ether extract.	Crude fibre.	Non-nitrogen- ous extract.
1 .....	79.5	78.4	88.3	52.9	86.4
2 .....	72.6	61.3	85.1	48.3	81.5

Sheep No. 1 digested the oats in the quantity given better than the large amount previously given (*loc. cit.*); sheep No. 2 digested more fat and crude fibre with the less amount of food, but not so much nitrogenous matter. It is probable that the nature of the individual sheep has a good deal of influence on the results. Much depends on the more or less complete chewing of the food, which, in this case although sufficiently nourishing, is very much wanting in bulk.

Experiments were next made in which the amounts of barley and rye digested by rabbits were determined. The results, together with those previously obtained, show that, under similar conditions, rabbits digest oats better than either barley or rye, as regards the two most important constituents, protein and fat. The difference in the percentage amounts digested is shown in the following table.

	Dry matter.	Organic matter.	Protein.	Fat.	Crude fibre.	Nitrogen free extract.	Ash.
Oats....	73.7	74.5	80.2	93.8	21.6	79.5	46.4
Barley..	84.0	85.4	67.7	86.3	25.1	91.2	51.2
Rye ....	84.4	85.4	63.0	76.3	18.5	91.2	34.4

The percentages obtained with barley are lower as regards proteids and fats than those given by Wolff for horses and sheep, whilst the non-nitrogenous extract is higher.

The value of oats is, compared with barley and rye, probably due in part to the greater digestibility of its proteids and fat.

N. H. M.

**Influence of Nitrogenous Manures on Grass.** By WOODS and PHELPS (*Bied. Centr.*, 1894, 90—91).—During 1890—92, nitrogenous manures were applied to unmanured land on which the crop growing consisted mainly of Timothy, smooth-stalked meadow and Fiorin grasses, whereby an increase of yield was obtained, whilst on a plot treated with minerals only, the clovers were increased. In addition to the increase of yield of hay produced by the nitrogen, the composition was also affected, as a higher percentage of proteids was obtained. On the plot manured with minerals (bone superphosphate and potassium chloride), the proteids were highest owing to the extra growth of the clovers. Excessive nitrogenous manuring is wasteful. Thus a plot which in the three years had received 84 kilos. of nitrogen yielded hay containing 139 kilos. of nitrogen, but another plot which had received 252 kilos. only returned 229·8 kilos. of nitrogen in the hay. E. W. P.

**Efficiency of the most important Preservatives of Stable Manure.** By H. IMMENDORF (*Journ. f. Landw.*, 41, 1—56).—The object of the experiments was to ascertain the effect of different calcium phosphates mixed with gypsum on the decomposing manure. For this purpose, damp meat-meal and blood-meal, mixed with ground grass or clover leaves, were treated with mixtures of the pure calcium salts mixed with gypsum, at a constant temperature of 30°, in a suitable apparatus, so that the changes could be observed, and gaseous products collected. The two substances, meat-meal and blood-meal, were selected rather than faeces and urine, owing to the greater ease with which accurate analyses of them can be obtained. After observing the effect of pure salts, experiments with commercial phosphatic manures were made. The apparatus was similar to that employed in earlier experiments (*Abstr.*, 1892, 374), but somewhat simpler.

In the first series, 15 grams of meat-meal mixture (containing 0·6848 gram of nitrogen) was used for each experiment; in the second series, 15 or 10 grams of blood-meal mixture (containing N = 0·666 and 0·444 gram). In both series, an equal weight of gypsum was added, besides the phosphates. In the third series, blood-meal mixture (20 grams) was mixed with a phosphatic manure alone. Tables are given showing the total and final amounts of nitrogen, the final amount of nitric nitrogen, and the final amounts of nitrogen as ammonia remaining in the material experimented on, and as that collected in the receiver, representing the loss which would take place in the open air. As regards changes in the total nitrogen, there was in no case (in the 20 experiments) a loss which could not be accounted for by the experimental error, and only in two cases a gain.

The table on page 211 shows the percentage of the nitrogen as ammonia which volatilised (which is the most important of the results), and the nitrogen as ammonia, which was fixed. Series I includes Nos. 1—8; Series II, 9—12; and Series III the rest.

The experiments 13 to 20 were made in pairs, alike as regards minerals added, but different as regards amount of ventilation, Nos. 14, 16, 18, and 20 being very slightly ventilated.

\*As regards nitric nitrogen at the end of the experiment, none was

	Nitrogen as ammonia.	
	Volatilised.	Fixed.
1. $\text{Ca}_3(\text{PO}_4)_2$ (3) .....	7.75	67.96
2. " (1.5) .....	9.43	59.46
3. $\text{Ca}_2\text{H}_2(\text{PO}_4)_2 \cdot (\text{P}_2\text{O}_5 = 1.8)$ .....	14.46	58.69
4. " ( " 0.9) .....	13.36	60.69
5. $\text{CaH}_4(\text{PO}_4)_2 \cdot (\text{P}_2\text{O}_5 = 0.6)$ .....	2.40	62.11
6. " ( " 0.3) .....	6.98	56.08
7. $\text{H}_3\text{PO}_4$ (0.551) .....	4.81	62.75
8. " (0.276) .....	11.84	63.60
9. $\text{Ca}_2\text{H}_2(\text{PO}_4)_2 \cdot (\text{P}_2\text{O}_5 = 1.8)$ .....	6.25	31.26
10. " ( " 0.75) .....	1.11	46.41
11. $\text{H}_3\text{PO}_4$ (0.455) .....	0.79	48.22
12. No phosphate .....	7.21	30.21
13. Containing $\text{P}_2\text{O}_5$ . (a) 8.99, (b) 3.33, (c) 1.92*	7.13	35.98
14. " " " " " "	1.29	34.20
15. " " (a) 9.62, (b) 2.96, (c) 6.2..	0.0	44.22
16. " " " " " "	0.0	40.54
17. " " (a) 8.11, (b) 1.72, (c) 6.2.	0.0	28.68
18. " " " " " "	0.0	22.79
19. " " (a) 13.83, (b) 1.73, (c) 11.5	0.0	48.52
20. " " " " " "	0.0	50.17

\* (a) total, (b) soluble in citric acid, (c) soluble in water.

found in experiments 1—12, and 16, whilst in the other experiments the following amounts, in percentages of total nitrogen, were found. (13), 1.39; (14), 0.40; (15), 0.60; (17), 1.94; (18), 1.23; (19), 1.59; (20), 1.15. The greatest amounts of nitrate were therefore formed when the ventilation was greatest. Its production is clearly not necessarily attended with a loss of nitrogen.

The results of the experiments show that the fixing power of gypsum for the ammonia of decomposing organic matter is considerably increased by free phosphoric acid and calcium monophosphate, that is, by phosphates soluble in water. Tricalcium and dicalcium phosphates are without effect. Superphosphate gypsum loses its fixing power to some extent through the water soluble phosphate becoming insoluble (soluble in citric acid), but not appreciably. It also seems to hinder the processes which give rise to the elimination of free nitrogen. Stassfurt salts suppress ammonia production to some extent, but seem to increase loss of free nitrogen. Kainite enriches the manure in potash and magnesia, and preserves the organic matter; but it is said to injure the hoofs of animals, and injures the manure for certain crops. Kainite and superphosphate gypsum gave good results, preventing both loss of ammonia and of



free nitrogen; the presence of superphosphate gypsum seems to compensate for the otherwise bad effect of the kainite. The addition of chalk to decomposing organic matter nearly always causes great production and loss of ammonia. N. H. M.

**Changes in, and Effects of, Irrigating Water.** By E. FRICKE, E. HASELHOFF, and J. KÖNIG (*Landw. Jahrb.*, 22, 801—849).—In former communications, the effects of various waters under various systems of meadow cultivation were discussed (*ibid.*, 6, 287; 8, 505; 11, 151; and 14, 177). In the present paper, the results of experiments with the same water on various soils are given.

**A. Irrigation with Ordinary Water.**—The experiments were conducted in large cases built of stone and cement. These were more than half filled with gravel, over which was the layer of sandy, loamy, calcareous, and peaty soil respectively. There were three cases for sandy soil irrigated (a) with the same amount of (Münster) water as the other cases; (b) twice the usual amount; and (c) the same amount of Münster water, but diluted with distilled water. This was to ascertain the effect of a pure water as compared with the Münster water alone, which is very rich in minerals. The temperature of the soils at different depths was observed, and there were arrangements for collecting drainage. The boxes were irrigated first in July, 1885 (the year after the grass was sown), and at five subsequent periods, of which the last was June, 1887. The irrigation was for about four days at a time. The surface drainage and that which passed through the soil were examined. Tables are given for each period, showing the amount and composition of the water applied, as well as the surface and other drainage from each soil. As regards the surface drainage, the amount of oxygen it contains is less than the original water, the decrease being greatest in the case of soils which contain the most organic matter. The carbonic anhydride and lime go together. The lime decreased considerably in the case of peaty soil, and slightly in the case of sandy soil, whilst in passing over calcareous and loamy soils the water became richer in lime. Magnesia, on the other hand, was taken up by the water from the peaty soil, and deposited to a slight extent in all the other soils. In every case, the water lost a good deal of nitric acid. The nutritive matters of irrigating water are not absorbed to any extent by the soil, but mainly by the plant directly, and the loss or gain in any constituent will depend on the wants of the plant and the presence of an excess or deficiency of the constituent in the soil. In warm weather, the surface drainage takes up more organic matter, but not always more carbonic anhydride, than in cold weather; in the case of peaty and sandy soils, which are poor in lime, the summer drainage contains less carbonic anhydride (and less lime) than the winter drainage. On the other hand, the surface drainage from the loamy and calcareous soils is richer in lime in warm than in cold weather. The quantity of nitrates is greater in summer drainage (except in the case of the loam) than in winter drainage; generally poor soils will respond most to irrigation, especially when vegetation is most active. Frequent but slight irrigation (to avoid surface drainage) during summer is recommended.

Night surface drainage contained more organic matter than the day drainage, probably due to a greater secretion of organic matter from the roots during the night. The peaty and sandy soil drainage contained less lime in the day time than in the night, whilst the reverse holds good in the case of the calcareous and loamy soils. The drainage through the soil generally behaves like the surface drainage. It contains less nitric acid than the surface drainage, showing that the deeper roots take up considerable amounts of food; and there is a general diminution of bases, that is to say, for 1 part of base the drainage contains more acid than the irrigating water and the surface drainage. The following numbers show the amount of acid to 100 base (1) in the surface drainage, and (2) in the drainage.

	Peaty soil.	Calcareous soil.	Loamy soil.	Sandy soil.
1 .....	167	166	165	169
2 .....	179	168	165	210

The relation in the water as applied was 100:164.

There is no definite relation between evaporation and kind of soil, evaporation depending chiefly on the amount of vegetation, sunshine, and the wind (compare Masure, *Landw. Jahrb.*, 1882, 191; Eser, *ibid.*, 1885, 208; Battelli, *Il Nuovo Cimento*, 1890, [3], 28, 247). Comparative experiments were made on the evaporation from a surface of water, from a soil containing 65 per cent. of the total amount of water it would hold, and from soil sown with grass. The relations in amount of evaporation were 100:65:202.

The amount and composition of the grass cut in 1886 and 1887 are given, as well as that in 1888 after irrigation with sewage water. As regards the crops of 1886 and 1887, the results show that the soils lost both nitrogen and potash, the amounts of these two constituents of the irrigating water being insufficient. Lime was deposited both in the peaty and sandy soils, but the calcareous and loamy soils both lost lime. In the case of magnesia, just the opposite takes place. Sulphuric acid was deposited in every case in excess of the amount found in the produce; it is probable that it was taken up by the roots as a reserve for future growth. The behaviour of lime and magnesia indicates a similar storing by the roots. The produce obtained under the influence of sewage water was richer in nitrogen, potash, and phosphoric acid than that of the two previous years.

The soils which benefit most in ordinary irrigation are the poor sandy soils; peaty soils are also improved, especially by water rich in lime (compare Fleischer, *Hannov. Landw. u. forstw. Zeit.*, 1884, 841; Egger, *Chem. Centralbl.*, 1887, 525, and *Trost. Ann. Soc. Geol. Belg.*, 11, 123).

**B. Irrigation with Sewage Water.**—These experiments were similar to those described above. The four different soils were employed. The sewage was mixed with tap water in the proportion 80:585. There were four applications from November, 1887, to March, 1889. The following table shows the average composition of the water as applied, and of the drainage, in milligrams per litre.

	Sewage water applied.	Drainage.			
		Peaty soil.	Cal- careous soil.	Loamy soil.	Sandy soil.
O <sub>2</sub> required for oxidation..	125.2	14.2	13.8	12.7	10.5
CO <sub>2</sub> .....	490.7	106.5	225.7	236.5	107.1
CaO .....	122.4	121.0	177.7	196.2	116.4
MgO .....	15.5	18.5	13.8	14.8	13.9
K <sub>2</sub> O .....	66.3	29.2	33.5	23.7	20.8
Na <sub>2</sub> O .....	99.2	56.5	55.7	59.0	54.1
Cl .....	134.4	111.9	91.4	97.6	92.8
HNO <sub>3</sub> .....	18.8	81.0	86.0	85.2	114.8
SO <sub>3</sub> .....	63.2	55.1	58.6	52.0	49.2
P <sub>2</sub> O <sub>5</sub> .....	14.0	0 - 1.3	0 - 1.3	0 - 1.0	0 - 0.5
Ammoniacal nitrogen ...	119.8	{ trace	{ trace	{ trace	{ trace
Organic nitrogen .....	31.0	{ -12.7	{ -12.4	{ -7.3	{ -3.1

Other experiments were made in which the sewage water was applied very frequently instead of at long intervals. The results of both sets of experiments show that the sandy soil is the most suitable, owing to its greater permeability for air. If insufficient air is present, a reduction of nitric to nitrous acid takes place, and loss both of nitrogen and sulphur. For complete oxidation of the sewage, vegetation is necessary, and it is important to avoid an excess of sewage. To utilise the nitrogen of the sewage, about twice as much phosphoric acid and three times as much potash are required as the sewage contains. The vegetation of 1 hectare of soil will take up, at the most, 300 kilos. of nitrogen, corresponding with the sewage from about 60 to 80 of the population.

*C. Irrigation with Impure Water containing Salt.*—The waters with which all four soils were successively irrigated in these experiments contained:—(1) nothing added; (2) NaCl, 0.1 per cent.; (3) CaCl<sub>2</sub>, 0.1 per cent.; (4) MgCl<sub>2</sub>, 0.1 per cent.; (5) FeSO<sub>4</sub>, 0.03 per cent.; (6) ZnSO<sub>4</sub>, 0.02 per cent.; and (7) CuSO<sub>4</sub>, 0.02 per cent. There was further dilution from rain. The application of common salt gave rise to an increased loss of lime, magnesia, and potash. Calcium chloride caused a deposition of lime in soil or plants and a loss of other bases (MgO, Na<sub>2</sub>O, and K<sub>2</sub>O). Magnesia, iron, zinc, and copper were all deposited, more or less, whilst the drainage removed other bases.

N. H. M.

## Analytical Chemistry.

**Estimation of Sulphur in Regenerated Gas-Purifying Material.** By F. MEYER (*Chem. Zeit.*, 17. 1319).—A few grams of the material is wrapped up in a filter and placed inside the bulb of a calcium chloride tube, which is then connected with a 150 c.c. round-

bottomed flask containing about 30 c.c. of carbon bisulphide. The top part of the tube is then connected with a reflux condenser. A Soxhlet's apparatus may, of course, be used instead of the calcium chloride tube. After heating the flask in a water bath of 80° for about an hour, the sulphur will be completely extracted. The flask is disconnected, the carbon bisulphide distilled off, and the residual sulphur finally oxidised by nitric acid and potassium chlorate.

L. DE K.

**Estimation of Free Acids in Salts of the Heavy Metals.** By F. HOFFMANN (*Chem. Zeit.*, 17, 1318—1319).—The author adds to the solution of the metallic salt, copper sulphate for instance, a very slight excess of potassium ferrocyanide, and then makes up to a definite bulk. After the precipitate has completely settled, an aliquot part of the liquid is syphoned off, and the free acid titrated with N/10 soda, using phenolphthalein as indicator. When the precipitated ferrocyanide is colourless, as in the case of lead, silver, or zinc, a moderate excess of ferrocyanide is not injurious, and the liquid need not be filtered before titrating. To be successful, the metals should be in the highest state of oxidation, the process failing, for instance, with ferrous sulphate.

L. DE K.

**Precipitation of Barium Sulphate in Presence of Silica and the Decomposition of Barium Sulphate by Hydrofluoric acid.** By J. F. SLEEPER (*Chem. News*, 69, 63—64).—It is shown that barium sulphate precipitated in the presence of sodium silicate is in no way contaminated; moreover, that barium chloride does not give a precipitate in a solution of sodium silicate. The suggestion of removing silica from barium sulphate by means of hydrofluoric acid is found to be untenable, inasmuch as mere evaporation with this acid is sufficient to decompose the sulphate, occasioning loss, which increases with the augmentation of the volume of the acid used: this decomposition is prevented by large, but not by small, quantities of free sulphuric acid.

D. A. L.

**Colorimetric Estimation of Iron.** By A. ZEGA (*Chem. Zeit.*, 17, 1564—1565).—For the estimation of iron in waters, the author recommends the following method. To 100 c.c. of the water (in which the iron has already been oxidised to the ferric condition) 1 c.c. of nitric acid (sp. gr. 1.35—1.40) and 5 c.c. of a 5 per cent. solution of potassium thiocyanate are added. The coloration develops rapidly, and does not darken on remaining. 100 c.c. of distilled water is then similarly treated, and a standardized solution of a ferric salt containing 0.01 milligram of iron per c.c. run in until the coloration produced is equal to that in the water under examination. The quantity of ferric solution added represents, of course, the quantity of iron in the water. In this way 0.01 milligram of iron per 100 c.c. of water is easily estimated.

L. T. T.

**Estimation of Nickel.** By J. F. SLEEPER (*Chem. News*, 69, 15—17).—To avoid the uncertainty incident to prevailing methods of

estimating nickel, the author has adopted the following modes of procedure.

Shot or plate nickel is broken up as far as possible, avoiding the introduction of adventitious iron, and 20—25 grams is dissolved by heating gently with 250 c.c. of dilute (1:1) nitric acid, the fumes being subsequently boiled off. The solution is made up to 2 litres and 50 c.c. evaporated to dryness with hydrochloric acid.

Mattes or ores are dissolved in aqua regia, and evaporated to dryness with hydrochloric acid; taking 1 to 5 grams, according to richness.

Speiss, 1 gram, is treated with aqua regia and frequent additions of a saturated solution of potassium bromide in water charged with excess of bromine, and is then evaporated to dryness with hydrochloric acid.

In these three cases the solutions, after evaporating to dryness with hydrochloric acid, are redissolved in this solvent, diluted, and the proportion of hydrochloric acid made up to one-eighth or one-tenth of the total volume.

Nickel oxide is reduced to an impalpable powder, dried at 130°, and 1 gram is heated gradually to, and then at, redness with sodium hydrogen sulphate, in a partially covered crucible, until action ceases, then, when sufficiently cool, about 2 c.c. of concentrated sulphuric acid is added, and the heating is resumed until the whole mass becomes liquid. When cool, it is dissolved in hot water (any residue being ignited and re-treated), and 7 to 10 c.c. of hydrochloric acid is added to the solution, the volume of which should be from 75 to 100 c.c.

A solution prepared by any of these methods is treated, while hot, with hydrogen sulphide, filtered, and the precipitate washed with hydrogen sulphide solution; the filtrate, after removing the hydrogen sulphide completely by boiling, is boiled for a further five or ten minutes with nitric acid, and, while boiling, is gradually and cautiously precipitated with excess of caustic soda, as free as possible from carbonate and alumina; the boiling is continued for 15 minutes longer, and after 15 minutes' standing on a water bath, filtration is proceeded with; the precipitate being thoroughly washed with boiling water, by digesting with it, as well as on the filter, before being dissolved in hot dilute sulphuric acid (1:15 or 20 of water); the total amount of sulphuric acid used in this and subsequent re-treatments should not, however, exceed 10 c.c. The solution is diluted to from 150 to 300 c.c., according to the quantity of iron present, and when cold is treated rapidly with excess of concentrated ammonia, allowed to settle, the supernatant liquid filtered off, the precipitate washed with water, redissolved in the dilute sulphuric acid and reprecipitated with ammonia, these operations being repeated two or three times if much iron is present. The combined filtrates are evaporated to 50 to 75 c.c., at a low temperature, to avoid drying up or the separation of any nickel salt, and the concentrated solution treated, as soon as convenient, with ammonia, using 5 c.c. in excess of that required to produce a blue colour, any precipitate is filtered off, redissolved, and reprecipitated, &c.; 25 c.c. of strong ammonia is added to the filtrate, which is diluted to 200 c.c. and electrolysed,

using cylindrical platinum electrodes supported at  $\frac{1}{8}$  to  $\frac{3}{16}$  of an inch above the bottom of the glass. There must be plenty of ammonia present; not too much sulphuric acid, and no nitrate, alumina, or iron. After use, the electrodes are cleaned by immersion in hot dilute nitric acid.

D. A. L.

**Estimation of Chromium in Chrome-Steel and Chrome-Iron Ore.** By J. SPÜLLER and S. KALMAN (*Chem. Zeit.*, 1360—1361: 1412).—Two grams of steel borings is dissolved in 16 c.c. dilute sulphuric acid (1—5) contained in a hemispherical dish of 300 c.c. capacity, and covered with a watch-glass. When effervescence has ceased, the glass is removed, rinsed with a little hot water, and the whole evaporated to dryness with constant stirring. When dry, the mass is calcined and then mixed in a silver basin with 4 grams of powdered sodium dioxide and 8 grams of sodium hydroxide. On heating the mass, frothing takes place at first, but this soon ceases when the contents are stirred with a silver spatula. The fusion is now continued for 15 minutes, when 4 grams of sodium dioxide is added; after 20 minutes' further heating another 2 grams of this substance is added; after the lapse of  $1\frac{1}{4}$  hour, the whole of the chromium is converted into sodium chromate. When cooled a little, the basin is freed from soot, placed inside a porcelain dish, and lixiviated with water. The further operations are the same as described in the authors' process for the estimation of chromium in ferrochrome (compare this vol., ii, 70).

Chrome-iron ore may also be analysed by direct fusion with the sodium dioxide mixture.

L. DE K.

**Electrolytic Estimation of Lead.** By A. KREICHGAUER (*Ber.*, 27, 315—318; compare Medicus, *Abstr.*, 1892, 1522).—The nitric acid, used in making the solution of lead nitrate to be electrolysed, should consist of 1 part of acid of sp. gr. 1.4 to 7 parts of water; the deposited lead dioxide should be washed twice with alcohol and dried for five minutes at 120°. It is slightly hygroscopic owing to the presence of a trace of nitric acid, which is difficult to remove; the amount of water taken up is, strange to say, independent of the weight of the dioxide.

C. F. B.

**Analysis of Phosphor-tin.** By C. A. LOBRY DE BRUYN (*Rec. Trav. Chim.*, 12, 262—267).—About 1 gram of the substance is introduced in small pieces (2—4 per gram) into a flask of 60—80 c.c. capacity; 40—50 c.c. of water is added, and the mouth of the flask covered by a funnel; 5 c.c. of purified liquid bromine is now added in 3 to 4 portions; about 1 c.c. of bromine is added at first, the flask being placed in a bath of cold water. Although the reaction proceeds with the production of flame, it must not be too rapid, and rise of temperature must be avoided, otherwise a gelatinous deposit of stannic oxide is produced. The whole operation of adding the bromine takes 5—10 minutes. If small particles of the substance remain unattacked, more bromine is added, the mixture gently heated on the water bath, and subsequently allowed to remain for some time. The solution is transferred to a porcelain capsule, the flask rinsed with

concentrated hydrochloric acid, the solution diluted with an equal volume of water, and the bromine is expelled by evaporation on the water bath. The concentrated hydrochloric acid serves to dissolve any stannic oxide. The solution must not be concentrated too much, or tin will be volatilised. The tin is estimated by precipitation as sulphide or by Classen's electrolytic method, whilst the phosphorus is estimated in the filtrate from the tin as magnesium pyrophosphate. A. R. L.

**Paraffin Estimations.** By R. HÖLAND (*Chem. Zeit.*, 17, 1473, 1483—1484).—The author has proved by a series of experiments that paraffin may be quantitatively separated from yellow oil (a product of the dry distillation of brown coal) by treating the sample with 10 times its bulk of commercial absolute alcohol and subsequently cooling in ice-cold water for about two hours. If, however, the amount of paraffin is less than 20 per cent., it is advisable to first remove the bulk of the oil by a fractional distillation.

The precipitated paraffin is collected on a weighed filter contained in a double funnel cooled with ice, and washed with cold alcohol. It is then freed from the bulk of alcohol by squeezing between blotting paper, and finally dried at 100° on a weighed watch-glass.

L. DE K.

**Analysis of Mixtures of Sperm Oil and Mineral Oil.** By C. A. LOBBY DE BRUYN (*Chem. Zeit.*, 17, 1453).—The author uses the process recommended by Allen and Thomson, but has made a slight modification. 5 grams of the sample is boiled for some hours with a solution of 2 grams of sodium hydroxide in 25 c.c. of absolute alcohol. The liquid is diluted with water and shaken twice with light petroleum, which is then washed with water and finally distilled off in a weighed flask. The contents are, after weighing, boiled with twice the volume of acetic anhydride. Complete solution takes place, but, on cooling, the mineral oil separates almost entirely, and can be readily removed from the acid. The author finds, however, that it retains a small proportion of acetic acid, which causes it to solidify in contact with metallic sodium; it is therefore necessary to agitate it with a weak alkali and again dissolve it in light petroleum. After distilling off the latter, the mineral oil is left in a pure state.

L. DE K.

**Partial Decomposition of the Constituents of Beer by Ebullition, and its Effect on the Estimation of Carbonic Anhydride and on the Detection of Sulphurous Acid.** By H. ELION (*Rec. Trav. Chim.*, 12, 255—261).—Among methods for the estimation of carbonic anhydride in beer, may be mentioned that of Schwackhöfer, improved by Langer and Schultze (*Zeit. ges. Brauw.*, 1879, 369). The method consists in driving out the carbonic anhydride with a current of air, but the last-named chemists contend that it is only possible to eliminate the last traces of carbonic anhydride by maintaining the liquid in ebullition for some time. The author ascribes the increased amount of carbonic anhydride found by prolonging the boiling to the decomposition of certain constituents of the beer.

Prior has shown (*Allg. Zeit. Bierbrau. u. Malzfab.*, 1891, 1281) that when hops are boiled with water, as in the process for detecting sulphurous acid, a small quantity of hydrogen sulphide is evolved, which complicates the process.

The author's results show that 5—10 minutes' ebullition is sufficient to eliminate all the carbonic anhydride from beer.

A. R. L.

**Detection and Estimation of Alkyl Groups attached to Nitrogen.** By J. HENZIG and H. MEYER (*Ber.*, 27, 319—320).—It is found that the alkyl iodide compounds of pyridine and quinoline decompose into base and alkyl iodide when heated, and that the hydriodides of bases which contain alkyl groups attached to the nitrogen atom behave in a similar manner. It is thus possible to estimate these groups by a modification of Zeisel's method.

No details of the process are given, as the method is still under investigation.

C. F. B.

**Rosaniline Hydrochloride as a Reagent for the Detection of Mineral Acids in Vinegar.** By G. GRIGGI (*Chem. Centr.*, 1893, ii, 1033; from *Chem. Zeit.*, 17, Rep., 276).—1 c.c. of the vinegar to be tested is placed in a flat porcelain basin, and a drop of an alcoholic solution of magenta (25 grams magenta in 100 c.c. of 90 per cent. alcohol) added. If only acetic acid is present, the colour is slightly intensified, but otherwise unchanged. In the presence of 1 per cent or more of mineral acid, the reddish-violet colour is changed to a dirty yellow.

L. T. T.

**Estimation of Formic Acid.** By A. LIEBEN (*Monatsh.*, 14, 746—754).—Formic acid is easily and accurately estimated by titration with standard potassium permanganate solution in the presence of sodium carbonate. The reaction takes place according to the equation  $3\text{KCHO}_2 + 2\text{KMnO}_4 = 2\text{MnO}_2 + 2\text{K}_2\text{CO}_3 + \text{KHCO}_3 + \text{H}_2\text{O}$ . An excess of sodium carbonate is without influence on the estimation, and if the solution is heated on the water bath, the manganese dioxide rapidly settles.

The author has examined the method devised by Scala (*Gazzetta*, 20, 393), which is based on the reduction of mercuric chloride to mercurous chloride. An accurate determination of formic acid is obtained by this method only when 5.6 times the theoretical quantity of mercuric chloride is employed and the mixture is heated at least 6—8 hours on the water bath.

E. C. B.

**Colour Reactions of Amines and Aldehydes without addition of Acids.** By E. NICKEL (*Chem. Zeit.*, 17, 1413).—Salts of aromatic amines, particularly those of aniline, give colour reactions with aldehydes. The author found, however, that the alcoholic solutions of the free bases also give colorations with some of the aldehydes. Experiments were made with the following amines—Aniline, ortho- and para-toluidine,  $\alpha$ - and  $\beta$ -naphthylamine, and piperidine; also with the following aldehydes—Anisaldehyde, salicylaldehyde, para-hydroxybenzaldehyde, piperonal, and vanillin.



Excepting piperidine, all these amines give, in presence of acids, plain yellow colorations with the aldehydes. Without the presence of acids, the author could not get a colour by means of  $\alpha$ -naphthylamine except with salicylaldehyde. The reaction of amines with hydroxyaldehydes or their derivatives is also different in the absence of acids. Aldehydes which contain a hydroxyl group, ortho- and para-hydroxybenzaldehyde, for instance, give, however, a yellow coloration without the addition of acid, although not so strongly and quickly as with acid. But aldehydes, such as anisaldehyde and piperonal, which contain alkyloxy-groups, do not give the reaction without addition of an acid.

Piperidine, which does not belong to the aromatic series and does not contain the group  $\text{NH}_2$ , but the imide group  $\text{NH}$ , behaves differently from the other amines. In the free state, it gives yellow colorations with salicylaldehyde or vanillin, which are destroyed by the addition of an acid. But with lignin, which is related to the aldehydes, it gives a reaction, even in the presence of sulphuric acid.

L. DE K.

## General and Physical Chemistry.

**Refractive Powers of some Organic Phosphorus Compounds.** By F. ZECCHINI (*Gazzetta*, 24, i, 34—42); compare Abstr., 1893, ii, 353).—The author has determined the refraction constants of a number of organic phosphorus compounds for the lines D and H<sub>a</sub>. The results obtained for the former ray are summarised in the following table, and are each the mean results of several determinations made under varied conditions.

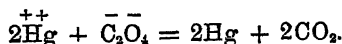
Substance.	Temp.	$P \frac{\mu_n - 1}{d}$ .	$P \frac{\mu_n^2 - 1}{a(\mu_D^2 + 2)}$ .	Atomic refraction of phosphorus.	
				From $\mu_D$	From $\mu_D^2$ .
PPhCl <sub>2</sub> .....	5·8—7·0°	81·10	46·17	17·47	8·79
PPh <sub>3</sub> .....	4·8—6·9	156·75	87·94	26·16	11·79
P(OEt) <sub>3</sub> .....	7·4—27·0	63·34	38·30	5·98	2·87
PO(OEt) <sub>3</sub> ...	5·7—28·1	69·09	41·79	7·50	4·17
P(OEt)Cl <sub>2</sub> ...	12·4—24·5	53·62	31·87	14·10	8·10
POPh(OH) <sub>2</sub> ..	—	60·07	35·61	5·07	2·61

The values given for triphenylphosphine were obtained in 7—11 per cent. benzene solutions. Two determinations of the constants for ethoxyphosphorous chloride were made with the pure substance, and one with an 8 per cent. benzene solution; slightly higher results were obtained in the latter case. The high atomic refraction of phosphorus in triphenylphosphine is analogous to that previously observed by the author with aromatic bases (this vol., ii, 2). The atomic refraction of the phosphorus in phenylphosphorous chloride (17·47 for  $n$ ) is somewhat greater than that in phosphorous chloride (14·89 for  $n$ ).

W. J. P.

**Photochemical Action in Solutions.** By M. ROLOFF (*Zeit. physikal. Chem.*, 13, 327—365).—The action of light on Eder's solution, that is, a mixture of solutions of mercuric chloride and ammonium oxalate, is first considered. The presence of a double salt is indicated by experiments on the alteration of the boiling point of water by the addition of the two constituents singly and together. The action of light on the solution causes the formation of mercurous chloride, and the amount so formed is determined under various conditions. The addition of substances which cause an increase in the dissociation causes an increase in the quantity of mercurous chloride formed and *vice versa*. The author therefore concludes that the undissociated molecules play no important part in the reaction. As the acceleration of the action is most marked by an increase in

the number of Hg and  $C_2O_4$  ions, the reaction is considered to be due to these, that is—



The mercury so formed then produces mercurous chloride by its action on the mercuric salt. As a photometric liquid, the solution is, however, subject to the disadvantages that it is relatively more sensitive in dilute than in strong solution, and that the carbonic anhydride formed by the reaction increases the sensitiveness.

The author then shows the probable existence of a compound,  $KBr_3$ , in a solution of bromine in potassium bromide solution, and examines next the action of bromine on oxalic acid—(1) in the dark; (2) under influence of light. In the first case the reaction velocity was found to decrease rapidly with the time. As potassium bromide is formed in the reaction, the decrease is probably due to the formation of the salt  $KBr_3$ , and hence the removal of some of the bromine. The ratio of the reaction velocities in light and in the dark was found to increase greatly with the time. The ratio was also increased by the addition of potassium bromide, and in this case did not vary with the time. As before, increase in the number of ions caused an increase in both cases in the velocity of the reaction. The author concludes, therefore, that the influence of light in this case is due to an increase in the activity of the Br and  $C_2O_4$  ions, and also to a raising of the activity of the  $Br_3$  group.

L. M. J.

**Electrodes for Resistance Determinations in Electrolytes.** By F. KOHLRAUSCH (*Ann. Phys. Chem.*, [2], 51, 346—350).—The author describes various forms of plane and cylindrical platinised platinum electrodes for dipping into liquids whose resistance is to be determined. One of the principal features of these electrodes is that the connections are made through double capillary glass tubes of 1.5 mm. bore.

J. W.

**Electrical Conductivity of Gases.** By F. BRAUN (*Zeit. physikal. Chem.*, 13, 155—162).—A number of different cases were investigated:—

(1.) Compound gases at the moment of formation. The only cases studied were mixtures of (1) nitric oxide and air; (2) chlorine and hydrogen, which were caused to unite by the influence of heat or diffused daylight. A Leyden jar battery of about 4000 volts E.M.F. was employed. No conduction was observable.

(2.) Gases during the time of explosion. A mixture of carbonic oxide and oxygen was employed, and a current from 7 to 20 small Grove cells was employed; in this case, there appeared to be undoubted conduction through the exploding gas.

(3.) Gases heated to high temperatures. The gases were heated in porcelain tubes to about 1000—1200°, and the current used was that from a Leclanché cell. Ammonium chloride and cadmium iodide conducted well; ammonia, iodine, and hydrogen chloride conducted, as did to a less extent hydrogen iodide, hydrogen bromide,

and probably mercuric oxide. No conduction was observed in the cases of carbonic anhydride, water, and nitric peroxide.

The paper closes with a short discussion of the electric charges of flames, which the author considers to be due to a separation of positive and negative ions.

The results in general confirm the experiments of De Hemptinne (Abstr., 1893, ii, 563).  
L. M. J.

**Laws of Galvanic Polarisation and Electrolysis.** By O. WIDDEBORG (*Ann. Phys. Chem.*, [2], 51, 302—345).—The author seeks to give a consistent exposition of the phenomena of galvanic polarisation on the following fundamental assumptions. The ions are driven by the active electromotive force towards the two electrodes, where they collect and generate new breaks in the potential, which, acting against the original electromotive force, regulate the current according to Ohm's law. All the ions that reach the electrodes, however, are not electrically active, but only a small proportion of them, the rest being neutralised, losing their ionic character, and contributing nothing to the sudden difference of potential. There is a limit to the gathering of the ions at the electrodes, and the relative amount which collects at any instant is smaller, the nearer the amount already collected is to the limit, being proportional to the difference between the limiting and actual values at the instant considered.  
J. W.

**Minimum Electromotive Force required to decompose Electrolytes.** By M. LE BLANC (*Compt. rend.*, 118, 411—412) and BERTHELOT (*ibid.*, 412—415).—Le Blanc points out that in 1891 (Abstr., 1891, 1405) he obtained results identical with those of Nourisson (this vol., ii, 178). Berthelot considers that both Le Blanc and Nourisson have only confirmed the conclusion at which he arrived in 1882 (*Ann. Chim. Phys.*, [5], 27, 58), namely, that the minimum electromotive force required to decompose an electrolyte is the sum of the heat absorbed by the separation of the acid from the base in dilute solutions, and the heat of decomposition into oxygen and hydrogen of the water by which the acid and base are dissolved, provided that the acid and base are neither oxidised nor reduced and that the electrodes are not attacked. This result is independent of any theory of dissociation into ions. Berthelot points out that the numerical values obtained by himself, Le Blanc, and Nourisson respectively, are practically identical.  
C. H. B.

**Fusibility of Isomorphous Mixtures of some Double Carbonates.** By H. LE CHATELIER (*Compt. rend.*, 118, 415—418).—Potassium carbonate and sodium carbonate, when fused with calcium, barium, or strontium carbonate, readily yield crystalline isomorphous double salts of the general formula  $M'O$ ,  $M''O$ ,  $2CO_2$ . They cleave easily, and when the plates are examined with convergent polarised light they are found to be negatively uniaxial, with the axis perpendicular to the plane of cleavage. They do not alter when exposed to

air, but decompose when heated above their melting points, the barium compounds being less stable than those which contain calcium.

Lithium carbonate will not combine with carbonates of the calcium group, but, on the other hand, forms double compounds with the alkali carbonates.

The following table shows the points of solidification of various mixtures, the numbers indicating the molecular proportions of each salt present in the mixture.

Na <sub>2</sub> CO <sub>3</sub> .....	1	1	1	—	—	1	1
K <sub>2</sub> CO <sub>3</sub> .....	—	—	—	1	1	—	—
CaCO <sub>3</sub> .....	1	—	—	1	—	0·5	0·5
SrCO <sub>3</sub> .....	—	1	—	—	—	0·5	—
BaCO <sub>3</sub> .....	—	—	1	—	1	—	0·5
Temperature of solidification.	790°	750°	740°	790°	800°	720°	660°
Na <sub>2</sub> CO <sub>3</sub> .....	1	—	—	0·5	0·5	0·5	—
K <sub>2</sub> CO <sub>3</sub> .....	—	—	1	0·5	0·5	0·5	—
CaCO <sub>3</sub> .....	—	—	0·5	1	—	—	0·5
SrCO <sub>3</sub> .....	0·5	—	—	—	—	—	—
BaCO <sub>3</sub> .....	0·5	—	0·5	—	1	—	0·5
Temperature of solidification.	720°	755°	760°	780°	780°	690°	—

The connection between the melting point and the composition can be represented by a triangular surface in the case of ternary mixtures, and by a square surface in the case of quaternary mixtures.

These results and those previously obtained (this vol., ii, 179) show that in all cases where the isomorphism can be decisively ascertained, the curves and the surfaces are perfectly continuous, and show no angular points.

When the temperature of the fused mixture remains constant during solidification, the crystals have the same composition as the mother liquor in which they are formed. Such mixtures in the case of alloys have been termed eutectic mixtures by Guthrie. Such mixtures show the minimum melting point, and for any pair of solids there is always one eutectic mixture. The same properties would seem to belong to the whole series of isomorphous compounds, the heat of formation of which is nil. In this case, the curve of the melting point is a right line connecting the melting points of the two constituents. With other mixtures, the melting point becomes lower and lower as crystallisation proceeds, the difference in composition between the crystals and the still liquid part being such that the composition of the latter tends towards the eutectic mixture, and finally reaches it.

C. H. B.

**Thermal Expansion and Compressibility of Solutions.** By G. TAMMANN (*Zeit. physikal. Chem.*, 13, 174—186).—The author observes that the thermodynamic surface of a solution approximately coincides with that of its solvent if for the former the zero of pressure be taken, not as 1 atmosphere, but as a higher value,  $\Delta k$ . This is expressed otherwise, thus if  $\phi(p.v.t.) = 0$  represent the thermo-

dynamic surface of the solvent,  $\phi(p + \Delta k, v, t) = 0$  represents that of the solution. In the simplest case  $\Delta k$  is independent of  $t$ . The section of the surface by planes perpendicular to the axis of pressure gives the isobars of the liquid. In the case of water, the isobars for high pressures fall above those for low, the reverse holding for other liquids. Corresponding with this is the fact that in solutions of the same substance in water, the isobars for high concentrations lie above those for low. A number of solutions are then compared, the data being obtained from the experiments of Marignac and Amagat. The pressures at which water has a similar expansion is found for solutions at five concentrations, and at four different temperatures in the cases of hydrogen chloride, sodium chloride and sulphate, and cane-sugar; the numbers obtained show that  $\Delta k$  is approximately proportional to the concentration, and increases slightly with the temperature. Calculations are also made from the determinations of Amagat on the lowering of the temperature of maximum density of water by pressure, and of Despretz and Rosetti on the similar lowering by solution of salts; the numbers for  $\Delta k$  agree satisfactorily with those previously obtained. The isobars of water cut one another at about  $125-130^\circ$ , hence, at this temperature, the isobars of salts of different concentration should cut each other and that of water; this is the case with sodium carbonate, but in other cases, owing to the increase of  $\Delta k$  with temperature, the temperature is lower than this. Also the coefficient of expansion of water at about  $55^\circ$  is the same for all pressures below 1000 atmospheres, and is equal to that of solutions at the same temperature, but for liquids in which  $\Delta k$  varies the point is slightly different.

The *isotherms* are next compared, and comparisons made by means of Tait's researches on the compressibility of salt solutions and of Amagat on the compressibility of water show satisfactory agreement.

L. M. J.

**Electrolytic Decomposition of Water.** By M. LE BLANC (*Zeit. physikal. Chem.*, 13, 161—173).—The author in this paper upholds the view of the primary decomposition of water, and replies to the objections brought forward by Arrhenius (*Abstr.*, 1893, ii, 441). The increase in the electrolytic decomposition of water by the addition of an electrolyte is explained, not by an increase in the degree of dissociation of the water, but in the capability of ion formation. He also explains the fact that hydrogen is not immediately liberated during the electrolysis of an alkali salt with a mercury cathode, by stating that the potassium ions give up their electricity to the mercury more readily than the hydrogen ions. That hydrogen ions are present in water is shown also by the fact that potassium reacts readily with water and not with paraffin. In the case of solution of various metallic cyanides in potassium cyanides, he points out that cadmium is easily separable, but platinum scarcely so, which is hard to explain on a secondary decomposition hypothesis, unless the electro-deposited platinum were soluble in potassium cyanide; this, however, he proves experimentally is not the case. He finally points out that the primary decomposition theory has the advantage of simplicity.

L. M. J.

**Hypothesis of Coloration of the Ions.** By G. MAGNANINI (*Gazzetta*, 24, i, 48—56).—Violuric acid has an affinity constant  $K = 0.00272$ . In an aqueous solution containing 1 gram-mol. of the acid in 256 litres, about 8 per cent. of the molecules present are dissociated into their ions; such a solution is colourless, or has, at most, a very slight yellow tint, and the ions, according to Ostwald's hypothesis (Abstr., 1892, 1137), are therefore practically colourless. The pure potassium, sodium, and ammonium salts of violuric acid have different colours when solid, but their aqueous solutions have the same red tint. The author has measured the coefficient of absorption of these three salts for aqueous solutions containing 1 gram-mol. in 50 and 100 litres, and confirms his previous observation (Abstr., 1892, 757; 1893, ii, 510) that the absorption coefficient is directly proportional to the number of gram-mols. of salt in solution. Further, the addition of a quantity of potassium nitrate to the solution, sufficient to diminish the electrolytic dissociation by 25 per cent. has no effect on the absorption.

Ostwald's hypothesis that, in an electrolyte, the dissociated part has a different colour from that of the non-dissociated part is therefore opposed to facts.

W. J. P.

**Stoichiometry of the Ions.** By G. BREDIG (*Zeit. physikal. Chem.*, 13, 191—288).—The author gives, firstly, a brief review of the position of our knowledge with regard to the ion migration. A table is next given for the conversion of the conductivity of a solution at various degrees of dilution into that at infinite dilution; this depends only on the product of the valencies of the ions, and not on their nature, and its validity is shown by a comparison of calculated numbers with those obtained by Kohlrausch. The exceptions, for instance, in magnesium salts, are referred chiefly to hydrolytic decomposition and to differences in the mode of ion formation. To the available data the author adds a large number of conductivity numbers obtained from his own experiments, more especially in the case of organic bases, the conductivity of about 150 substances having been determined by means of an alternating current and telephone; aqueous solutions of different strengths were employed in most cases, and the results carried to infinite dilution. About 300 different substances were thus available for discussion. As follows theoretically, the difference  $\mu_{100} - \mu_{32}$  was approximately constant. Such substances as aniline chloride, which are partially decomposed in aqueous solution, were examined in a solution of the base itself. From these data, using the value of Nernst and Loeb for the velocity of the silver ion ( $a_{Ag} = 59.1$ ), the velocities of about 300 ions are calculated, and then, by means of the above-mentioned table, the conductivity of the substance at  $\mu_{128}$ ; in almost all cases the agreement between these numbers and those found experimentally, is very good. The ion velocities are in all cases given in mercury units; so that for conversion into C.G.S. units they should be multiplied by  $110 \times 10^{-7}$ . From the results obtained the author points out the following relations.

The velocity of the elementary ions is a periodic function of the

atomic weight, the curve being also very closely analogous to that for internal friction.

In complex ions, the velocity is largely an additive property; isomeric ions of analogous constitution have equal velocities; and to a continuous additive change in the composition of the ion corresponds a continuous, but decreasing, change in the velocity.

In general, a retarding effect is produced by the replacement (i) of H by Cl, Br, I, Me,  $\text{NH}_2$ , or  $\text{NO}_2$ ; (ii) of any element by an analogous element of higher molecular weight (exc. O and S), of  $\text{NH}_3$  by  $\text{H}_2\text{O}$ ; of  $(\text{CN})_x$  by  $(\text{C}_2\text{O}_4)_x$ , by the change of amines into acids; of sulphonic acids into carboxylic acids, acids into cyanamides, dicarboxylic into monocarboxylic acids, and by monamines into diamines.

The additive effect is, however, largely influenced by constitution. Thus in metamerides the velocity increases with the symmetry of the ion, especially with increase in the number of C—N unions.

To the paper is also added an addendum showing the accordance of the author's numbers with those recently published by Kohlrausch (this vol., ii, 79).

L. M. J.

**Non-electrolytic Dissociation in Solutions.** By M. WILDERMANN (*Ber.*, 26, 2881—2897).—The author has in a previous paper (*Abstr.*, 1893, ii, 509) advanced the view that in solutions the dissolved substance is contained in the condition of complex (higher) and simple (lower) molecules and of the products of dissociation of these, the dissociation of the higher molecules being non-electrolytic, and that of the lower molecules being electrolytic in character. This view evidently agrees with that of Arrhenius in assuming in electrolytes the existence of simple molecules and their ions, but goes further, and adds to these the presence of higher molecules and their products of dissociation in smaller or greater quantity. It is likewise maintained that all dissolved substances in all solvents whatsoever and at all strengths of the solution, undergo electrolytic dissociation.

The electrical conductivity of solutions was considered in the former paper (*loc. cit.*), and the views above given were found to afford an explanation of facts which the theory of electrolytic dissociation alone was incapable of explaining. In the present paper, the depression of the freezing point is considered, and here also the assumption of the existence of complex molecules and non-electrolytic dissociation is found to afford a general explanation of the observed facts.

H. C.

**Applications of Raoult's Law at the Boiling Point of Solutions.** By O. ŠULE (*Ber.*, 27, 594—595; compare *Abstr.*, 1893, ii, 406).—A solution of rhamnose in ethylic alcohol is levorotatory, whilst in isopropylic alcohol or in water it is dextrorotatory. Further, the molecular weight of rhamnose as determined ebullioscopically, is too great in its solutions in methylic and in ethylic alcohol, but normal in isopropylic alcohol and in water. But all the lower alcohols behave in the same way ebullioscopically with regard to such a substance as water; hence the differences observed above must have their source in the rhamnose. Probably they are caused by the formation of



rhamnose alkyl oxides which are stable in alcoholic solution; it is known that rhamnose hydrate, for example, is decomposed by amylic alcohol, water distilling over; and, in fact, the ethyl rhamnoside (rhamnose ethoxide) of Fischer was found to be levorotatory in alcoholic solution. C. F. B.

**Exact Method for the Determination of the Reduction of the Freezing Point.** By E. H. LOOMIS (*Ann. Phys. Chem.*, [2], 51, 500—523) and by F. KOHLRAUSCH (*ibid.*, 524—528).—Loomis' method for cryoscopic determinations is that described in a former paper (*Abstr.*, 1893, ii, 261), and details of experiments with the substances mentioned in that communication are given. In the case of sodium chloride, the numbers obtained are in excellent agreement with those of Jones, and differ from those of Pickering in showing no breaks in the continuity of the freezing-point curve.

Kohlrausch draws attention to the fact that the close agreement between the results of Loomis and of Jones in the case of sodium chloride does not hold for the other substances examined by the two observers. Possible sources of error in Jones' results are suggested, and particular attention is drawn to the wavy character of some of his freezing point curves, a point which Pickering (*Trans.*, 1894, 293) has also commented on. H. C.

**Proportionality between the Reduction of the Freezing Point and the Osmotic Pressure.** By S. ARRHENIUS (*Ann. Phys. Chem.*, [2], 51, 493—499).—The proportionality which the author maintains exists between the reduction of the freezing point and the osmotic pressure has recently been called in question by Dieterici, who bases his arguments upon observations of W. Fischer. It is shown that the untrustworthiness of Fischer's experimental work invalidates Dieterici's conclusions, and that, substituting observations by Juhlin, excellent agreement with the author's theory is obtained. H. C.

**Nature of Osmotic Pressure.** By G. MAGNANINI (*Gazzetta*, 24, i, 81—90).—The author replies to a paper by Naccari, in which the latter defends his experiments on the osmotic pressure of sugar solutions; the fallacy of the experiment has been previously pointed out by the author, by Le Blanc, and in a note to the abstract of Naccari's first paper on the subject (*Abstr.*, 1893, ii, 513). W. J. P.

**Cryoscopy of the Hydrate  $H_2SO_4 \cdot H_2O$ .** By R. LESPIEAU (*Bull. Soc. Chim.*, [3], 11, 71—76).—A large quantity of the monohydrate of sulphuric acid was fractionally crystallised until the melting point rose to, and remained stationary at,  $8.53^\circ$ , a temperature identical with that observed by Pickering. The extreme variations noted in the temperature of a mixture of crystals and liquid during 48 hours was  $0.04^\circ$ . The only experimental difficulty is that due to superfusion, crystallisation being difficult to induce and tedious to carry out.

The constants in the equation  $Mx/p = cx + K$ , where  $x$  = lowering of freezing point,  $p$  = percentage of dissolved substance,  $M$  = mole-

cular weight of dissolved substance,  $a$  = constant for solid,  $K$  = constant for solvent, were determined for acetic, pyruvic, and uric acids.

$$\begin{aligned} a &= 1.2, -2.7, 13.3, \\ K &= 48.1, 47.5, 48.0. \end{aligned}$$

$K$  may, therefore, be taken as 48.

The value of  $K$ , calculated from the latent heat of fusion, is 49.5, taking Berthelot's value, 31.7 Cal., and 39.3, taking Pickering's value, 39.9 Cal.

Thus, from the cryoscopic point of view, this molecular compound behaves as an individual. JN. W.

**Degree of Affinity of Some Insoluble Mineral Bases.** By J. MYERS (*Rec. Trav. Chim.*, 12, 315—329).—The relative affinities of certain insoluble mineral bases were determined from the rate of action of the insoluble base silver oxide on solutions of their nitrates. Decinormal solutions were taken, and most of the experiments were carried out at the boiling points of these solutions. The nitrates of zinc, copper, lead, and cadmium were first examined. Some difficulty was experienced with the lead and cadmium solutions, owing to the formation of basic salts, but it was eventually found that the order of affinity (basicity) of the hydroxides is as follows, beginning with the weakest:— $\text{Cu}(\text{OH})_2$ ,  $\text{Zn}(\text{OH})_2$ ,  $\text{Cd}(\text{OH})_2$ ,  $\text{Pb}(\text{OH})_2$ . Experiments with magnesium nitrate proved unsuccessful, owing to secondary reaction and formation of a compound,  $\text{Mg}(\text{OAg})_2$ , which is deposited in the form of light yellow needles upon the sides of the vessel containing the solution. Calcium and barium nitrates behave in a similar manner. The author finds, however, that silver nitrate is completely decomposed by magnesium oxide at the ordinary temperature. The affinities observed are not, as might be expected, proportional to the relative amounts of electrolytic dissociation in the nitrates examined, and in so far contradict the accepted view of the identity of chemically and electrically determined affinities.

H. C.

**Affinity Coefficients of Bases.** By G. BREDIG (*Zeit. physikal. Chem.*, 13, 288—326).—A large number of affinity coefficients were determined, chiefly of bases the conductivity of whose chlorides the author had previously determined (this vol., ii, 226). The measurements were all made electrolytically by use of the telephone and alternating current. The values for  $\mu_\infty$  were calculated from the previously obtained numbers for the ion velocities, using the value  $a'_{\text{OH}} = 167$ . The affinity coefficient is given by the equation

$$k = \frac{m^2}{v(1 - m)},$$

where  $m$  is the degree of dissociation =  $\mu_\infty/\mu_s$ , and  $v$  is the volume of solution per gram molecular weight.

The results show that the quaternary organic bases are the strongest and the tertiary the weakest. The bases of phosphorus, arsenic, antimony, sulphur, and tellurium are very strong; those of

tin and mercury very weak. In metameric diamines the base is stronger the further removed are the amido-groups.

A number of very weak bases were examined in solutions of the hydrochloride, and the value  $k_3/k_4$  determined; that is, the strength of the base referred to that of water. The ratio multiplied by  $2.29 \times 10^{-16}$  gives the affinity constant of the base.

The author upholds the accuracy of the electrolytic method, more especially with regard to objections raised against it by Lellmann (Abstr., 1892, 1269; 1893, ii, 407).  
L. M. J.

**Affinity Coefficients of Organic Bases.** By E. LELLMANN and A. LIEBMANN (*Annalen*, 278, 141—152).—Continuing the experiments of Lellmann and Gortz on aniline (Abstr., 1893, ii, 407), the authors find that this base has a fixed value for its affinity coefficient which varies, however, under certain influences. It is hardly probable that all these influences have been ascertained, but the authors have qualitatively proved the effect of agitating the solution during the experiment, and also the action of magnetism. They intend to repeat their observations quantitatively. It is noteworthy that the influence of agitating the solution raises the affinity coefficient, whilst the influence of magnetism lowers it.  
A. R. L.

**Affinity Coefficients of Acids.** By E. LELLMANN and A. LIEBMANN (*Annalen*, 278, 152—173).—It has been shown by Lellmann and Schliemann (Abstr., 1893, ii, 408) that determinations of the affinity coefficients of acids in aqueous solution by the spectrophotometric method give results incompatible with Guldberg and Waage's law. Abnormal results are also obtained when 96 per cent. alcohol is used as the solvent, but the values, unlike those obtained in aqueous solution, increase with the concentration. Results quite in accord with the law of mass action are obtained when 50 per cent. aqueous acetone is used as the solvent.

Numerous determinations of the affinity coefficient of phenylacetic acid are recorded, the barium salt, as before, being examined. Great differences in the values were observed, the causes of which are unknown, but may, perhaps, be the same as suggested in the case of aniline (last abstract). The authors have made a series of determinations of the electrical conductivity of phenylacetic acid and its barium salt, and, comparing their results with the values obtained by the spectrophotometric method, they conclude that there is no proportionality between electrical conductivity (dissociation) and chemical activity. They also reply to the criticisms of Nernst (Abstr., 1893, i, 449).  
A. R. L.

**Laboratory Apparatus.** By A. BIDET (*Compt. rend.*, 118, 478—481).—A constant level siphon (Fig. 1) is obtained by attaching a lateral tube, O' S, to an S tube a little above the lower bend. The lower branch is placed in the vessel in which the constant level is to be maintained, and the water is brought in through the upper vertical branch, A. When the level of the liquid in the vessel falls below the

lower bend, the siphon acts in the direction BO; if it rises higher, the siphon acts in the direction BS.

The *safety tube* (Fig. 2) allows of the introduction of an acid, whilst any gas that is evolved escapes through the lateral tube. If the pressure inside the vessel becomes high, the liquid in the cylindrical bulb is driven up into the funnel and the gas escapes through the bent tube without projecting the liquid from the funnel; when the pressure falls, the liquid runs back from the funnel into the bulb.

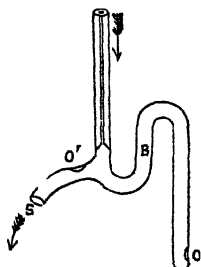


Fig. 1.

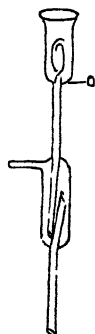


Fig. 2.

*Condenser with Internal Circulation.*—A wide tube, closed at one end, is fused into the lower end of a wide condenser tube, so that a narrow, annular space is left between them. The inner tube is fitted with a cork carrying two tubes, one for the entrance, the other for the exit of cold water. One end of the outer tube is connected with the distilling flask and the lower end with the receiver. If necessary, a third tube may be added, giving an outer circulation of water as well.

*Commutator for Condensers* (Fig. 3).—This consists of an external

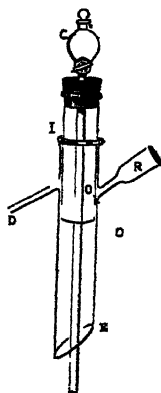


Fig. 3.

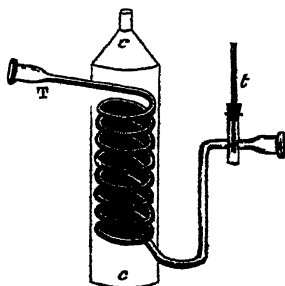


Fig. 4.

tube, E, carrying two tubulures, one of which, R, communicates with the reflux condenser, whilst the other, D, can be attached to a descending condenser. The internal tube, I, turns in such a manner that the aperture, O, can be brought opposite either R or D. The apparatus is attached by means of a cork to the vessel containing the liquid, and the vapour can be sent into either condenser by altering the position of the aperture O. A funnel, thermometer, &c., can be passed through the inner tube, as shown in the figure.

A convenient *superheater* (Fig. 4) for vapours can be constructed of a helix of copper tube, with a core of metallic gauze, the whole being surrounded by a metal cylinder with an open conical top. The flame of a Bunsen burner is allowed to play on the gauze in the centre of the helix, and it is easy to maintain a temperature of  $300^{\circ}$ . The temperature of the issuing vapour is indicated by the thermometer, t, placed in the vertical side tube. C. H. B.

**Lecture Experiment: Electrolysis of Hydrochloric acid.** By L. MEYER (*Ber.*, 27, 850—853).—The method usually adopted for the electrolysis of hydrochloric acid as a lecture experiment invariably yields less chlorine than hydrogen, even when the liquid has been previously saturated with chlorine. This is due to the fact that in the ordinary form of apparatus (Hofmann's) the chlorine is collected under a gradually increasing pressure, and has to pass up through a long column of the acid, which dissolves more and more of the gas as the experiment proceeds and the pressure on the chlorine increases. This is largely prevented in the apparatus described by the author, in which the chlorine does not pass through the acid, but only comes in contact with its surface. This is effected by collecting the gases in tubes which are connected by ground joints with the two limbs of the H-shaped apparatus containing the electrodes, the gas entering at the top of the collecting tubes. A. H.

## Inorganic Chemistry.

**Hydrates of Hydrogen Bromide.** By S. U. PICKERING (*Phil. Mag.*, [5], 36, 111).—A series of density determinations were made with solutions containing from 65 per cent. of hydrogen bromide downwards, and the results examined graphically. They gave indications of two not very well marked breaks at strengths corresponding with a tri- and tetra-hydrate. On making a series of freezing-point determinations, both these hydrates were isolated in the crystalline condition, the former melting at  $-48^{\circ}$ , the latter at  $-55.8^{\circ}$ . With the exception of the previously known dihydrate, no other hydrate was isolated. There are some grounds, however, for regarding the existence of a pentahydrate as probable, although solutions of about that strength did not solidify at  $-80^{\circ}$ .

For the hydrates of hydrogen chloride see *Ber.*, 26, 277, and also *Proc.*, 1893, 45; for those of hydrogen iodide, together with a list of the various hydrates, isolated in the cases of the three haloïd acids, see this vol., ii, 11.

S. U. P.

**Action of Dry Ammonia on Dry Carbonic Anhydride.** By R. E. HUGHES and F. SODDY (*Chem. News*, 69, 138—139).—Ammonia, carefully dried by means of soda-lime, solid caustic soda, and ignited lime, and carbonic anhydride, carefully dried by means of sulphuric acid and phosphoric anhydride, are found not to react when mixed together.

D. A. L.

**Preparation of Pure Potassium Iodate.** By M. GRÜGER (*Zeit. angew. Chem.*, 1894, 13).—40 grams of pure potassium permanganate is dissolved in 1 litre of hot water. 20 grams of potassium iodide, dissolved in a little water is added, and the whole heated in a boiling water bath for 20—30 minutes, when the excess of permanganate is reduced by the cautious addition of alcohol. The filtrate is acidified with acetic acid, and evaporated to about 50 c.c. The mother liquor is poured off, and the crystals of potassium iodate are washed with strong alcohol, and dried.

L. DE K.

**Behaviour of Sodium Peroxide towards acids.** By J. TAFEL (*Ber.*, 27, 816—824).—Sodium peroxide evolves oxygen when strongly heated or on treatment with water at ordinary temperatures. By the action of alcoholic hydrochloric acid at about 0°, a white powder is formed, which, after purification, undergoes decomposition at 100°, oxygen being evolved. This substance is a mixture, or a compound, of 2 mols. NaCl and 1 mol. NaO·OH. It decomposes gradually at the ordinary temperature, dissolves in ice-cold water without evolution of gas, and the solution has a strongly alkaline reaction. On acidifying with sulphuric acid, the solution reduces potassium permanganate at the ordinary temperature, oxygen being liberated; on boiling the acid solution, it is decomposed somewhat slowly. On acidifying the alkaline solution with hydrochloric acid, instead of sulphuric acid, chlorine is evolved on heating, and potassium iodide is decomposed at the ordinary temperature. Sodium peroxide dissolves in alcoholic acetic acid, and a compound is deposited which resembles the preceding substance in appearance and general properties, but its aqueous solution is neutral. On heating the solid, oxygen and water are eliminated and sodium acetate remains; the compound is, therefore, either sodium acetate with hydrogen peroxide, instead of water of crystallisation, or, more probably, a mixture of sodium acetate with the compound NaO·C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, the acetic derivative of the hydrate NaO·OH. Failure to detect the formation of hypochlorous acid, or of sodium hypochlorite, by the action of alcoholic hydrochloric acid on the acetate, leads the author to suggest the formulæ, O·Na·OH and O·Na·OAc, for the hydrate and acetate respectively. The consequences resulting from the assumption of a tervalent sodium atom will be considered subsequently. Full analytical details of the compounds are included in the paper.

J. B. T.

**Trihydrate of Lithium Iodide.** By A. N. THIRSOFF (*J. Russ. Chem. Soc.*, 25, 467—472).—The salt,  $\text{LiI} \cdot 3\text{H}_2\text{O}$ , first prepared by Rammelsberg, melts at  $72^\circ$ , and can be crystallised unchanged from absolute alcohol. At  $120^\circ$  it loses water slowly, 1 mol. being given up much more readily than the other two. J. W.

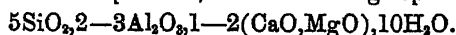
**Lithium Fluoride.** By C. POULENC (*Bull. Soc. Chim.*, [3], 11, 15—17).—Lithium fluoride may be obtained in a crystalline form by fusing the amorphous compound with a mixture of potassium hydrogen fluoride and potassium chloride. On slowly cooling the melt, and washing away the flux with water, the fluoride is obtained as a mixture of regular octahedra and small, nacreous spangles derived from the latter. The spangles are alone formed if the potassium chloride is omitted from the flux.

Lithium fluoride is intermediate in character between the alkali fluorides and those of the alkaline earths. It is sparingly soluble in water, but insoluble in 95 per cent. alcohol. It is easily decomposed by nitric and sulphuric acids, but with difficulty by aqueous hydrochloric acid, although at a red heat it is completely decomposed by gaseous hydrogen chloride, and partially by steam. It does not form a fluorochloride. It melts at about  $1000^\circ$  in an atmosphere of hydrogen fluoride, and partially volatilises at  $1100$ — $1200^\circ$ . J.N. W.

**Action of Hydrogen on Cæsium Oxide.** By N. BEKETOFF (*J. Russ. Chem. Soc.*, 25, 433—434).—Anhydrous cæsium oxide, when brought into contact with hydrogen, at once darkens, with slow absorption of the gas. A trace of moisture serves to make the action recommence after it has ceased in dry hydrogen. According to the author, the action is expressed by the following equation:— $2\text{Cs}_2\text{O} + \text{H}_2 = 2\text{Cs} + \text{CsOH}$ . J. W.

**Silver Aurochloride.** By F. HERRMANN (*Ber.*, 27, 596—597).—This substance,  $\text{AgAuCl}_4$ , may be obtained by dissolving 4 parts of gold in aqua regia, evaporating the solution nearly to dryness, adding first a solution of 1 part of silver in dilute nitric acid, and then 10 parts of the strongest nitric acid, evaporating almost to dryness, and repeatedly adding very strong nitric acid to the residue, and evaporating it. It is thus obtained in lustrous, orange-red needles with yellow streak; it darkens in colour superficially when exposed to sunlight in moist air, decomposes when heated at about  $230^\circ$ , and is only slowly decomposed by water, but rapidly by dilute hydrochloric acid and by ammonia. C. F. B.

**Composition of some Mortars.** By O. REBUFATT (*Gazzetta*, 24, i, 28—33).—The author has analysed a specimen of mortar taken from the base of some Roman pillars about 2,000 years old, at about 11.5 metres under the sea surface; a mortar about 20 years old, taken from a pier, was also examined. Both mortars are trachytic, and very similar in composition, the latter being represented by



W. J. P.

**Scott's Cement.** By G. GIORGIS (*Gazzetta*, 24, i, 23—28).—The author is examining the "Scott's Cement" prepared by heating calcium sulphate with lime, but publishes no conclusions as to its nature in this preliminary note. W. J. P.

**Graphochemical Calculations, with especial Reference to Soda Lime Glasses.** By E. NICKEL (*Zeit. physikal. Chem.*, 13, 366—372).—A further application of the author's method of calculation. (Abstr., 1892, 1158, and 1893, ii, 119.) L. M. J.

**The Precipitation of Metals from Dilute Solutions.** By F. MYLLUS and O. FROMM (*Ber.*, 27, 630—651).—*A Wet Method of forming Metallic Alloys.*—Silver-zinc is obtained when a solution of silver sulphate is gradually added to water in which a zinc-plate is placed, the silver solution being added at such a rate that not more than 0.03 gram of silver is present per litre. No evolution of hydrogen is observed, and the product is precipitated as a black, amorphous mass, which is, however, sometimes contaminated with white silver crystals, especially if the solution is too strong. The product contains from 75.3—48.2 per cent. of silver and 24.7—51.8 per cent. of zinc. When rubbed with an agate rod, it acquires a white metallic lustre. When treated with concentrated silver nitrate, it yields white crystalline silver and zinc nitrate; with strong acids, it yields silver, hydrogen, and a zinc salt. It precipitates copper and gold from their solutions. It is oxidised slowly by exposure to air, and with faintly acid hydrogen peroxide yields white silver. With bromine water, it yields white silver and silver bromide; and chromic acid converts it into zinc and silver chromates.

*Copper-zinc* is obtained in a similar way to the silver-zinc. A small quantity of hydrogen is evolved during the action, and a small quantity of basic zinc sulphate precipitated. It is a black, amorphous powder, containing from 59.4—50 per cent. of copper and 40.6—50 per cent. of zinc. When rubbed, it acquires a yellow metallic lustre, and is essentially a brass. It behaves like brass towards dilute acids. With concentrated copper solution, it forms crystalline copper and zinc sulphate, precipitates gold and silver from their solutions, and yields hydrogen and a residue of crystalline copper when treated with acids.

*Gold-zinc*, obtained in a similar way to the above, forms black, spongy flocks, containing equal weights of the two metals.

Those metals which, like platinum, iridium, and palladium, have a great affinity for zinc, are precipitated from their dilute solutions as black precipitates containing large quantities of zinc. Metals which have less affinity for zinc behave differently. A very dilute solution of lead chloride or acetate gives a grey precipitate which contains only 3—5 per cent. of zinc, a part of which is probably present as oxide. Tin and cadmium solutions behave in the same way.

*Silver-cadmium* is obtained as a black, spongy precipitate containing 54.4—35.2 per cent. of silver and 45.6—64.8 per cent. of cadmium. Under pressure it acquires a white, metallic lustre, and is similar to silver-zinc in chemical properties.



*Copper-cadmium* is obtained as a greyish-black, crystalline precipitate, and has the composition  $\text{Cu}_2\text{Cd}$ . When treated with concentrated hydrochloric acid, a violent evolution of hydrogen takes place, but the residual copper still contains a trace of cadmium.

*Gold-cadmium* is a lead-grey crystalline precipitate, having the composition  $\text{AuCd}_3$ . It remains unaltered by exposure to air, decomposes solutions of the noble metals, is scarcely acted on by dilute acids, and, when treated with concentrated hydrochloric acid, yields hydrogen, gold, and cadmium chloride. When heated, it is converted into gold-monocadmium  $\text{AuCd}$  (Heycock and Neville, *Trans.*, 1892, 906).

Cadmium precipitates the metals of the platinum group from dilute solution in a spongy form containing large quantities of cadmium. With dilute lead solutions, it gives a crystalline precipitate consisting of pure lead.

*Copper-tin*. A tin plate in contact with a very dilute neutral or acid copper solution becomes covered with a grey coating of crystals having a metallic lustre; the liquid at the same time becoming turbid, owing to the formation of a basic tin salt. The product has the composition  $\text{Cu}_3\text{Sn}$ ; it is fairly stable towards acids, and is decomposed by hot concentrated hydrochloric acid with evolution of hydrogen, leaving a residue of red copper which, however, still contains tin. The authors point out that an alloy of the two metals of the composition  $\text{Cu}_3\text{Sn}$  has been shown to have the properties of a definite chemical compound (Laurie, *Trans.*, 1888, 104; Riche, *Compt. rend.*, 55; Mallet, *Fehling's Handwörterb.*, 3, 1227; Lodge, *Phil. Trans.*, 1879; and Calvert and Johnson, *Phil. Trans.*, 1858).

Tin precipitates from dilute silver solutions a black compound containing a large quantity of tin; it is, however, very unstable, and contains also tin oxide. With dilute gold solutions, tin gives a dark precipitate which evolves hydrogen with concentrated hydrochloric acid. Gold-purple containing tin oxide is always formed at the same time. With platinum solutions, tin gives black and yellowish-brown precipitates.

From dilute copper solutions, lead precipitates a reddish-brown compound containing lead, which gives hydrogen when treated with hydrochloric or acetic acid. A plate of lead in dilute silver solution at first becomes covered with a dark film, but crystalline silver is very soon formed. *Gold-lead* is, however, easily formed, and is a deep black precipitate which gives hydrogen and gold when treated with acids. *Platinum-lead* is obtained as a crystalline precipitate; *Iridium-lead* is also easily obtained.

The authors were unable to separate an alloy by the action of copper on dilute silver solutions, as crystalline silver is precipitated at the same time. With gold solutions, they obtained a black, spongy compound containing copper, and a similar compound with platinum solutions. By the action of mercury on dilute silver solutions a beautiful crystalline amalgam is obtained. Iron acts on dilute neutral solutions of the metals with evolution of hydrogen, and alloys could not be obtained with copper, silver, or gold; with platinum solutions

however, a precipitate is obtained which contains iron, and evolves hydrogen when treated with hydrochloric acid.

The alloys described above are most easily prepared by shaking the positive metal in the form of powder with a solution of the negative metal. They undergo double decomposition like other insoluble chemical compounds; thus gold-zinc, when shaken with a cadmium solution, yields gold-cadmium and a zinc salt; and the compound Cu<sub>2</sub>Zn, obtained by shaking zinc-dust with a solution of copper sulphate, when shaken with a solution of tin chloride yields copper-tin, Cu<sub>3</sub>Sn, and zinc chloride.

The black metallic precipitates obtained by electro-deposition are not identical with the above, although they are very similar. The black metallic deposit obtained from silver solutions acts in the same way as zinc-silver towards concentrated silver solution, dilute acids, and oxidising agents. When silver is deposited from a dilute, faintly acid, sulphate solution on a wire cathode with a large current density, a black flocculent substance is obtained which is suddenly converted into white crystalline silver with evolution of hydrogen. Black silver deposited from a neutral solution contains no hydrogen, or only a very minute quantity. Platinum, cadmium, and zinc can also be deposited in a black porous condition, but lead cannot.

The authors have examined the behaviour of copper hydride under certain conditions. With a solution of potassium cyanide, it gives cuprous cyanide, potassium hydroxide, and hydrogen; with copper sulphate, it gives copper and free sulphuric acid. It may be cautiously heated to 140°, without completely decomposing. It cannot be prepared by the action of zinc on an acid solution of copper sulphate, the compound obtained under these conditions being copper-zinc (*Schoor. Arch. Néerland.*, 12, 96). The black precipitate formed at the zinc pole of a Daniell's cell is also copper-zinc, and when the cell is exhausted copper-zinc is also deposited at the copper pole. The authors were unable to obtain copper hydride by electro-deposition.

E. C. R.

**Allotropic Changes of Iron under the Influence of Heat.** By G. CHARPY (*Compt. rend.*, 118, 418—421).—When iron is in the  $\alpha$ -condition it shows a rectilinear break in the curve representing the elongation as a function of the load, but the modification  $\beta$  shows no such break. The relative proportions of  $\alpha$  and  $\beta$  in a given bar can be estimated by comparing the length of the rectilinear break in its curve with that of a bar which has been completely converted into the  $\alpha$ -modification. The author has applied this fact to the investigation of the condition of iron that has been heated to various temperatures in an electric muffle, and cooled by suddenly immersing it in a cold liquid.

The results obtained show that the allotropic modification of iron takes place spontaneously at a sufficiently high temperature, and can be made permanent by sudden cooling; it therefore plays an important part in the operation of tempering. The transformation takes place more quickly, the higher the temperature; with steel containing 0.8 per cent. of carbon, the change does not begin after heating for an hour at 700°, or for five minutes at 750°, but it is complete after

heating for 30 minutes at  $750^{\circ}$ , or for five minutes at  $800^{\circ}$ . Other steels yield similar results, and it follows that in metallurgical operations it is necessary to take into account not only the temperature, but also the time during which the temperature is maintained.

When iron is tempered, it undergoes a change which can also be produced by deformation in the cold, but there is no evidence to show whether this change is the cause of the hardening. C. H. B.

**Higher Oxides of Nickel.** By E. D. CAMPBELL and P. F. TROWBRIDGE (*J. Anal. and Appl. Chem.*, 7, 301—307).—The authors communicate the results of several experiments they have made to obtain nickel in a higher state of oxidation. The *modus operandi* was to precipitate nickel sulphate with sodium carbonate in presence of bromine at various temperatures. The degree of oxidation was ascertained by treating the products with potassium iodide and hydrochloric acid and titrating the liberated iodine.

From the experiments made, the authors conclude that the higher oxides of nickel are unstable compounds, and that an oxide higher than  $\text{Ni}_2\text{O}_3$  can be obtained. They have not, however, succeeded in obtaining nickel dioxide,  $\text{NiO}_2$ . L. DE K.

**Purification of Thorium Oxide.** By C. BÖTTINGER (*Zeit. anorg. Chem.*, 6, 1).—Advantage is taken of the fact that a solution of thorium oxalate in warm ammonium oxalate is precipitated by strong hydrochloric acid; the ignited precipitate yields a pure oxide. A prescription for making cones for the Welsbach light is given.

A. G. B.

**Sulphur Compounds of Thorium.** By G. KRÜSS (*Zeit. anorg. Chem.*, 6, 49—56; compare Abstr., 1893, ii, 574).—By heating thorium oxide in carbon bisulphide at a red heat, thorium oxysulphide,  $\text{ThOS}$ , coloured black with carbon, is obtained. The same compound is the product of heating ammonium thorium chloride, potassium thorium chloride, and thorium oxychloride respectively, in hydrogen sulphide. It has a light, brown colour. A. G. B.

**Complex Acids. Tungstovanadates and Ammonium Phosphomolybdates and Arsenomolybdates.** By C. FRIEDHEIM (*Zeit. anorg. Chem.*, 6, 11—26, 27—34; compare Abstr., 1893, ii, 282, 378, 472).—When a mixture of sodium paratungstate and sodium vanadate is fractionally crystallised, the salts  $5\text{Na}_2\text{O}, 6\text{WO}_3, 3\text{V}_2\text{O}_5 + 38\text{H}_2\text{O}$  (Abstr., 1890, 14),  $6(\text{Na}_2\text{O}, 2\text{WO}_3), \text{Na}_2\text{O}, \text{V}_2\text{O}_5 + 29\text{H}_2\text{O}$ , and  $7(\text{Na}_2\text{O}, 2\text{WO}_3), \text{Na}_2\text{O}, \text{V}_2\text{O}_5 + 66\text{H}_2\text{O}$  are obtained. The aqueous solution of the first of these salts, sodium ditungstosquivanadate, is precipitated by barium chloride, silver nitrate, calcium chloride, and potassium chloride; the composition of the precipitate in each case is discussed (compare Rosenheim, Abstr., 1889, 762). When potassium salts are substituted for sodium salts in the method of preparation, no crystalline products are obtained. Ammonium salts yield ammonium paratungstotriivanadate, with evolution of ammonia.

The salts produced by the action of molybdic anhydride on ammonium arsenate and ammonium phosphate, and of ammonium

molybdate on ammonium arsenate and phosphate, have been analysed; their formulæ are discussed. A. G. B.

**Action of Heat on Ruthenium Alkali Nitrites.** By A. JOLY and E. LEIDTÉ (*Compt. rend.*, 118, 468—471).—The orange-red salt, very soluble in water, formed in neutral solution by adding the calculated quantity of potassium nitrite to a solution of ruthenium chloride has the composition  $\text{Ru}_2(\text{NO}_2)_6, 4\text{KNO}_2$ , and the yellow salt, only slightly soluble in water, and formed in an alkaline solution in presence of excess of alkali nitrite, has the composition  $\text{Ru}_2\text{O}(\text{NO}_2)_4, 8\text{KNO}_2$ ; it crystallises with  $\text{H}_2\text{O}$ , but becomes anhydrous at  $100^\circ$  (compare Abstr., 1890, 17).

**Ruthenium Sodium Nitrites.**—When a solution of sodium nitrite is gradually added to a solution of ruthenium chloride at  $60$ — $80^\circ$  until the liquid is neutral, an orange-red solution is obtained, which, on cooling, deposits the compound  $\text{Ru}_2(\text{NO}_2)_6, 4\text{NaNO}_2, 4\text{H}_2\text{O}$  in orange-yellow, dichroic, monoclinic prisms, very soluble in water, from which they can be repeatedly recrystallised without decomposing. When heated with dilute hydrochloric acid, the salt yields the nitrosochloride  $\text{Ru}(\text{NO})\text{Cl}, 2\text{NaCl}$ ; when mixed with potassium hydroxide and saturated with chlorine, it gives off vapours of ruthenium peroxide. From 5 to 6 kilos. of this salt were obtained from 60 kilos. of iridium residues, rich in ruthenium, and hence sodium nitrite is of great service in the extraction of the metal from substances in which it is present in small quantity.

When the potassium salt  $\text{Ru}_2\text{O}(\text{NO}_2)_4, 8\text{KNO}_2$  is heated at  $360^\circ$  or  $440^\circ$  in a vacuum, there is sudden and almost explosive decomposition, nitrogen and nitrogen peroxide being evolved, and the residue, when treated with water, yields a solution of alkali nitrite quite free from ruthenium. The insoluble black residue has the composition  $\text{K}_2\text{O}, 3\text{Ru}_2\text{O}_5$ , and its formation confirms the acidic character of per-ruthenic acid (Abstr., 1892, 282).

The sodium salt at  $360^\circ$  or  $440^\circ$  yields the compound  $\text{Na}_2\text{O}, \text{Ru}_2\text{O}_5$ , which cannot be a mere mixture of the alkali oxide and the ruthenium oxide, since the latter would decompose at  $440^\circ$ . At a dull red heat, the nitrite yields the oxide  $\text{RuO}_2$ , which retains only a trace of alkali after being washed with boiling water. If the temperature is so high that the alkali nitrite fuses, the greater part of the ruthenium is converted into the ruthenate  $\text{K}_2\text{RuO}_4$ . O. H. B.

## Mineralogical Chemistry.

**Hydrocalcite from Wolmsdorf.** By B. KOSMANN (*Jahrb. f. Min.*, 1894, i, Ref. 260—261, from *Gluckauf*, 28, No. 38).—In the marble quarry at Wolmsdorf, near Landeck, a stalactitic cavern was recently laid bare, in which the roof was covered with a white consistent mass. This was found to be a hydrated calcium carbonate having the com-

position represented by the formula  $\text{CaCO}(\text{OH})_4$ . For this mineral, the author suggests the name of hydrocalcite. B. H. B.

**Taraspite from Vulpera, Switzerland.** By C. v. JOHN (*Jahrb. f. Min.*, 1894, i, 257—258; from *Verhandl. k. k. geol. Reichsanst.*, 1891, 3).—The author has investigated taraspite from Vulpera, a mineral similar to the miemite of Zepče. It is derived from serpentine, and has the composition of a normal dolomite in which some of the magnesia is replaced by iron, and in which, as in the serpentine, some nickel is present. Taraspite therefore should be classed with miemite. Its composition is as follows:—

$\text{CaCO}_3$	$\text{MgCO}_3$	$\text{FeCO}_3$	$\text{NiO}$	Insol. in HCl.
54.78	42.83	2.02	0.14	0.82

B. H. B.

**New Minerals from the Sjö Mine, Sweden.** By L. J. IGELSTRÖM (*Zeit. Kryst. Min.*, 22, 467—472).—The author describes some additions to the numerous new antimony minerals found by him in the Sjö manganese Mine during the last 10 years.

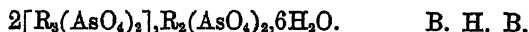
1. *Lamprostibian* was found in June, 1893, and has been named from *λαμπρός* and *stibium*. It resembles highly laminated, specular iron ore, from which it is distinguished by its brighter colour. In thick pieces, it is opaque; but in thin layers, it is transparent with a blood-red colour. Its hardness is about 4. It is brittle and non-magnetic. Qualitative analysis shows it to be an anhydrous ferrous and manganous antimonate.

2. *Elfstorpite* is a hydrated, pale yellow, translucent, manganous arsenate, occurring in crystalline patches and in crystals probably of the rhombic system. Its name is derived from the Elfstorp Iron-works in the vicinity of the Sjö Mine.

3. *Ohloroarsenian* occurs as minute, yellowish-green crystals of high lustre, apparently monosymmetrical or triclinic. It seems to consist of manganous arsenite.

4. *Rhodarsenian* is a red, transparent mineral occurring in globules in arseniopleite. Analysis gave results in accord with the formula  $(10\text{RO}, \text{As}_2\text{O}_5) + 10(\text{RO}, \text{H}_2\text{O})$ , in which RO is  $\text{MnO}, \text{CaO}, \text{MgO}$ .

As an appendix to this paper, the author describes two new minerals from the same mine, descriptions of which he has already published in Swedish (*Geol. Fören. Förhandl.*, 14, 307). These are *basiliite*,  $(\text{Mn}_2\text{O}_3)_4, \text{Sb}_2\text{O}_5 + 7\text{Mn}_2\text{O}_3, 3\text{H}_2\text{O}$ , and *sjögrufvite*,



B. H. B.

**Powellite from a new Locality.** By G. A. KÖNIG and L. L. HUBBARD (*Zeit. Kryst. Min.*, 22, 463—466).—The material examined was found in the autumn of 1892 in the 14th level of shaft No. 8 of the South Hecla Mine, Michigan. It has a hardness of 4.5, a sp. gr. of 4.349, a pale, bluish-green colour, and a vitreous lustre. Analysis gave the following results.

	MnO <sub>3</sub> .	WO <sub>3</sub> .	CaO.	MgO.	Fe <sub>2</sub> O <sub>3</sub> .	SiO <sub>2</sub> .	Cu
I.	65.74	4.50	27.41	—	—	—	—
II.	67.84	1.65	27.30	0.16	0.96	1.52	trace

B. H. B.

**Chemical Composition of Chondrodite, Humite, and Clinohumite.** By S. L. PENFIELD and W. T. H. HOWE (*Amer. J. Sci.*, [3], 47, 188—206).—The authors show that the minerals of the humite group are not identical in composition, and that they can be expressed by the following formulæ.

Chondrodite .....	Mg <sub>3</sub> [Mg(F·OH)] <sub>2</sub> [SiO <sub>4</sub> ] <sub>2</sub> .
Humite .....	Mg <sub>5</sub> [Mg(F·OH)] <sub>2</sub> [SiO <sub>4</sub> ] <sub>3</sub> .
Clinohumite .....	Mg <sub>7</sub> [Mg(F·OH)] <sub>2</sub> [SiO <sub>4</sub> ] <sub>4</sub> .

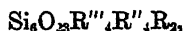
The variation in composition is intimately connected with the crystallisation, the three minerals forming a crystallographic series in which the vertical axes increase from chondrodite to clinohumite. By dividing the vertical axes by 5, 7, and 9 respectively, the quotients become practically identical, and it is an interesting fact that the divisors correspond with the number of magnesium atoms in the formulæ deduced.

B. H. B.

**Axinite from Bourg d'Oisans, Dauphiné.** By P. JANNASCH and J. LOCKE (*Zeit. anorg. Chem.*, 6, 57—71).—In continuation of a series of tourmaline analyses (Abstr., 1889, 472), the authors have made two careful analyses of axinite from Dauphiné with a view to affording information regarding the constitution of silicate-borates. The mean results of the two analyses were as follows.

SiO <sub>2</sub> .	B <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.
42.88	6.02	18.24	0.62	7.10	1.06	19.89	2.23
				K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
				0.11	0.36	2.14	100.65

These results are in accord with the empirical formula



or  $\text{Si}_5\text{O}_{23}(\text{Al},\text{B})_4(\text{Ca},\text{Fe},\text{Mn},\text{Mg})_4\text{H}_2$  (compare this vol., ii, 55).

B. H. B.

**Moldavite from Radomilic, in Bohemia.** By C. v. JOHN (*Jahrb. f. Min.*, 1894, i, Ref., 266—267; from *Jahrb. k. k. Geol. Reichsanst.*, 39, 473—476).—The author has analysed the moldavite or bottlestone from Radomilic (described by Woldrich in 1888) with the following results.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	Ignition.
I.	82.28	10.08	—	2.03	2.24	0.98	2.20	0.28	0.06
II.	77.75	12.90	—	2.60	3.05	0.22	2.58	0.26	0.10
III.	77.69	12.78	2.05	1.45	1.26	1.15	2.78	0.78	—

I, light green variety; II, dark green; III, light brown. The high percentage of potash is noteworthy. Although the nature of

the occurrence appears to indicate a natural origin, the author is unable to decide whether the mineral is a natural or an artificial product.

B. H. B.

**Minerals from York Haven, York Co., Pa.** By C. H. EHRENFELD (*J. Anal. Appl. Chem.*, 7, 4—5).—An analysis of weathered *stilbite* gave the following results.

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	K <sub>2</sub> O.	H <sub>2</sub> O.
52.07	22.11	12.17	trace	13.57

The mineral occurs on the exposed surfaces of the rock as a white mass, without the least sign of crystallisation. Hardness 2. It is readily gelatinised by hydrochloric acid.

An analysis of *chabasite* gave the following results.

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	K <sub>2</sub> O.	H <sub>2</sub> O.
50.69	19.46	7.28	1.38	21.32

The mineral occurs in small, almost cubical rhombohedra, 0.5 mm. to 2 mm. square, and translucent. Specific gravity, 2.18. It is not gelatinised by hydrochloric acid.

An analysis of *augite* showed—

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	H <sub>2</sub> O.
51.27	10.01	9.11	13.23	13.60	1.64

It occurs near to or mixed with *stilbite*, and has a dark bronze-green colour, shining lustre, and crystalline structure. Specific gravity, 3.008.

*Sphalerite* occurs as a thin coating between layers of blue limestone, but the author could not get it in a sufficiently pure condition for the purpose of analysis.

L. DE K.

**Topazolite and Melanite.** By M. PINERS (*Zeit. Kryst. Min.*, 22, 479—496).—The determination of minerals of the garnet group presents many difficulties. Under the head of lime-iron garnet, for example, there are classed two entirely different members of the group, topazolite and melanite. In order to definitely determine the composition of these two members, the author has made careful analyses of topazolite from the Mussa Alp, in Piedmont; from Wurlitz, in the Fichtelgebirge; and from a new locality in the Southern Tyrol; as well as of melanite from the Burgumer Alp, in Pfätsch; from the Margola, in the Southern Tyrol; and from a new locality near Zermatt. The results show that topazolite is essentially a pure lime-iron garnet, free from titanate anhydride, occurring, unless darkened by a foreign pigment, as pale yellow or greenish-yellow crystals. Melanite, on the other hand, is the name that should be given to titaniferous lime-iron garnets, as indicating the fact that they are invariably black.

B. H. B.

**Serpentine from Brewster, New York.** By G. FRIEDEL (*Zeit. Kryst. Min.*, 22, 580—581; from *Bull. Soc. Fran. Min.* 14, 120).—Among the numerous pseudomorphous forms in which serpentine

occurs at the Tilly Foster iron mine, near Brewster, New York, there are compact masses that have a perfect cubical cleavage, and also in places an octahedral cleavage, the cleavage-planes exhibiting a pearly lustre. The author, however, comes to the conclusion that the phenomenon is not one of cleavage, but that the entire mass consists of a network of rhombic lamellæ having the chemical composition of serpentine, which cross at the angles of the octahedron and cube, and whose interstitial space is filled with a dense substance of the same composition.

B. H. B.

**Meteorites of Knyahinya and Hainholz.** By E. PRIWOZNIK (*Jahrb. f. Min.*, 1894, i, Ref., 274—275; *Österr. Zeit. Berg. Hutt.*, 1892, No. 39).—The stone meteorite that fell on June 9, 1866, at Knyahinya, in Hungary, contained 5·03 per cent. of magnetic constituents, and 94·97 non-magnetic. The latter was pulverised, and treated with hydrochloric and nitric acids, with the result that 47·56 per cent. passed into solution (Analysis I), whilst 52·774 remained insoluble (Analysis II). The analytical results were as follows.

	SiO <sub>2</sub> .	CaO.	MgO.	Fe.	Ni.	FeO.	Al <sub>2</sub> O <sub>3</sub> .	Cr <sub>2</sub> O <sub>3</sub> .	Na <sub>2</sub> O.	S.
I.	88	2·9	18·3	2·4	0·32	11·60	1·14	—	—	2·10
II.	33·4	3·0	9·1	—	—	4·6	1·8	0·004	0·87	—

The metallic grains isolated by means of the magnet from the decomposed aerolite of Hainholz, near Paderborn, gave on analysis

Fe.	Ni.	Co.	P.	C.	Total.
92·4	7·0	0·2	0·298	—	99·898

B. H. B.

## Physiological Chemistry.

**New Animal Calorimeter.** By J. S. HALDANE, W. H. WHITE, and J. W. WASHBOURN (*J. Physiol.*, 16, 123—139).—The calorimeter described embodies the principle of D'Arsonval's. The test experiments described, including some in which animals were used, show it to be accurate, and its accuracy can at any time be easily tested. Moreover, it can be used simultaneously as an accurate respiration apparatus. For a full description of the instrument, reference must be made to the original paper, where an illustration exhibits the principal points in its construction. The action of the calorimeter is as follows. In one copper chamber the animal is placed; in the other hydrogen is burnt, both chambers being shut. The heat given off from the animal warms its chamber, and thus increases the pressure of the air in the space between the two upper walls of its chamber. This would lead to movement of the fluid (oil of erigeron) in a manometer, one limb of which communicates with the air space of the one chamber, the other with that of the other chamber. In the other chamber, hydrogen is kept burning, and the pressure of the



air in its surrounding space is thus increased, and tends to move the fluid in the manometer in the opposite direction. If the fluid in the manometer remains stationary, the amount of heat given off by the animal is equal to that produced by the burning hydrogen; and during an experiment the manometer is kept stationary by turning up or down the hydrogen flame. The amount of hydrogen burnt is estimated, and knowing the heat of combustion of hydrogen, it is possible to calculate the heat produced by its combustion in the experiment, which is equal to that given off by the animal.

For testing purposes, each chamber is furnished with a jet of hydrogen. W. D. H.

**Influence of Time on the Absorption of Carbonic Oxide by Blood.** By N. GRÉHANT (*Compt. rend.*, 118, 594—595).—When a dog is made to breathe artificially a mixture of air and carbonic oxide containing 100 c.c. of the latter in 100 litres, after half an hour the blood contains 6.0 c.c. of carbonic oxide in 100 c.c.; after an hour, 9.2 c.c.; after two hours, 10.0 c.c.; and after two hours and a half 9.3 c.c. With the proportion of carbonic oxide specified, the volume absorbed by the blood becomes practically constant after an hour.

With a mixture containing only 10 c.c. of carbonic oxide in 100 litres, the law of absorption is different and the proportion of carbonic oxide in the blood gradually increases. After half an hour, 100 c.c. contain 1.42 c.c. of the gas; after an hour, 2.05 c.c.; after an hour and a half, 2.9 c.c.; after two hours, 3.15 c.c.; after two hours and a half, 3.6 c.c. C. H. B.

**Behaviour of the Phosphorus in the Digestion of Casein.** By E. SALKOWSKI (*Exper. Stat. Record*, 5, 428; from *Centr. Med. Wiss.*, 1893, 385—386).—It is frequently stated that in the pepsin digestion of casein the phosphorus is not dissolved, but is separated as insoluble paranuclein. The author finds that much of the phosphorus is dissolved by the digestive fluid, and that only about 15 per cent. is contained in the paranuclein. It may therefore be assumed that the phosphorus has a definite function. N. H. M.

**Absorption of Iron.** By A. B. MACALLUM (*J. Physiol.*, 16, 268—297).—The experiments consisted in administering iron compounds to animals, and by microchemical methods determining whether the absorbing cells of the alimentary tract take up any. Inorganic compounds were found to be absorbed. If the dose is small, absorption occurs only in a small part of the duodenum adjacent to the pylorus. With larger doses the area increases. With small doses, the iron of the unabsorbed salt is precipitated by bile and other secretions as hydroxide, which is not assimilable; large doses first destroy the alkalinity of these liquids, so that the excess of salt remains in solution and undergoes absorption.

The intestinal epithelium cells transfer the absorbed iron at once to the underlying elements, but if the dose is large the epithelial cells will still be found containing some. Although some of the sub-

epithelial leucocytes appear to carry it into the general circulation, probably the more important agent in the transference is the blood-plasma.

Marfori's albuminate and the commercial "peptonate" of iron, when administered to guinea pigs, stimulate the leucocytes to invade the epithelial layer of the villi.

Of the organic iron compounds belonging to the chromatin or nuclein class, that present in egg-yolk (Bunge's hæmatogen) undergoes absorption. For several days after feeding, the cytoplasm of the liver cells yields marked evidence of an iron-containing chromatin. The mode of absorption of the yolk chromatin is obscure, and appears to be connected with the absorption of the fat with which the iron compound is closely associated in yolk.

W. D. H.

**Influence of Ichthyol on Metabolism.** By O. HELMERS (*Virchow's Archiv*, 135, 135—146).—Ichthyol influences the metabolism of proteid in the human body only in a slight degree. Its action, such as it is, is to diminish the decomposition and favour the assimilation.

About a third of the sulphur in the drug circulates in the body juices, and is excreted finally in the urine. That which passes from the body by the fæces has also in part circulated in the body, and is excreted by the intestinal glands.

W. D. H.

**Dietetic Value of different Kinds of Bread.** By G. MENICANTI and W. PRAUSNITZ (*Zeit. Biol.*, 30, 328—367).—Bread made with yeast leads to smaller formation of fæces than bread made with the same flour with leaven; wheat bread is also better in this direction than rye bread, whilst bread made with a mixture of wheat and rye flour is intermediate. Bread made from the decorticated grain also leads to a less abundant excrement. This excrement appears to be for the most part due to the residues of intestinal juice, and not so much to unabsorbed food. The harder the bread, and the coarser the flour, the greater is the amount of intestinal juice secreted. The finer German meals used contain particles averaging 0.1 to 0.14 mm. in diameter, but reference to other writers shows that the size varies considerably in different parts of the country.

W. D. H.

**Influence of Sugar and of Smoking on Muscular Work.** By V. HARLEY (*J. Physiol.*, 16, 97—122; and *Proc. Roy. Soc.*, 54, 480).—The experiments were performed with Mosso's ergograph, and show that the periods of digestion, as well as the kinds of food, have a marked influence on voluntary muscular energy; but, irrespective of this, there is a periodical diurnal rise and fall in the power of doing work, the *minimum* being about 9 A.M., the maximum about 3 P.M. Regular muscular exercise increases the size and power of the muscles, and delays the onset of fatigue. The amount of work performed on sugar alone is almost equal to that obtained on a full diet, but fatigue comes on sooner. Sugar acts as a source of muscular energy when taken alone, or in addition to other articles of diet. Moderate smoking may have a slight influence in diminishing the

power of doing muscular work, but it stops neither the morning rise nor the evening fall.

W. D. H.

**Asparagine in the Organism.** By J. LEWINSKY (*Chem. Centr.*, 1894, i, 53—54; from *Centr. Med. Wiss.*, 1893, 709—718).—In the quantitative estimation of amido-acids, such as asparagine, by Schultze's method, in which half the contained nitrogen is eliminated as ammonia, and the other half as aspartic acid, concentrated hydrochloric or sulphuric acid has hitherto been used; the present research, however, shows that it is better to employ 20 per cent. acid.

After removing the proteid matter from blood or organs, asparagine or aspartic acid can be precipitated by copper acetate; the copper precipitate contains 60 to 80 per cent. of the amido-acid. From the copper precipitate, the percentage of asparagine can be reckoned from the amounts of copper and nitrogen. The estimation of asparagine is not possible by this method in organs, on account of the varying amount of extractive nitrogen they contain.

After feeding a dog on asparagine (4 to 6 grams per kilo. of body weight), asparagine could not be found in the liver, spleen, or carotid blood. The blood, however, shows an increase of extractive nitrogen up to the fifth hour after the dose, when the absorption maximum appears to occur. In six hours, two-thirds of the asparagine given is excreted as urea.

W. D. H.

**Proteids of Spleen and Thyroid.** By F. GOURLAY (*J. Physiol.*, 16, 23—33).—A full account of experiments, already published in a preliminary communication (*Abstr.*, 1893, ii, 425).

W. D. H.

**Effect of Calcium Phosphate in Food on the Ash of Milk.** By J. NEUMANN (*Exper. Stat. Record*, 5, 639—640; from *Milch Zeit.*, 22, 701—704).—Three cows had each 100 grams of calcium phosphate added to their usual food—brewer's grains (22·5 kilos.), hay (4 kilos.), oat straw (2 kilos.), and salt (20 grams). The experiment lasted about 5 weeks. The average percentage amount of lime and phosphoric acid in the milk, before and after adding the phosphate to the food, was as follows:—

	CaO.	P <sub>2</sub> O <sub>5</sub> .
Without calcium phosphate.....	0·1479	0·1960
With        "        "        ".....	0·1592	0·2132

An experiment which lasted less than two weeks gave no definite results.

The results indicate a slight increase in both constituents, both percentage and absolute, when calcium phosphate is given with a food already containing sufficient amounts of ash constituents. The increase is only apparent after three or four weeks, which perhaps accounts for the negative results obtained by others. The production of so-called "phosphate-milk" with a high percentage of phosphate is considered impossible (compare *Abstr.*, 1893, ii, 582).

N. H. M.

**Combinations of Chlorine in Urine.** By A. BERLIOZ and E. LÉPINOIS (*J. Pharm.*, 29, 282—296).—In addition to mineral chlorides, the urine contains organic compounds containing chlorine. This fact is of importance in determining the variations in the amount of chlorine in healthy and pathological urines; and still more valuable would be the result if it were possible to simultaneously examine the chlorine compounds in the gastric juice. W. D. H.

**Odour of Benzole acid.** By J. PASSY (*Compt. rend.*, 118, 481—482).—Benzoic acid, prepared by various methods, has no odour while in the crystalline condition, but if volatilised in the vapour of water, or dissolved in dilute alcohol, or if a solution in a 0.6 per cent. aqueous solution of sodium chloride is inhaled in the form of spray, the characteristic odour is at once perceived. These results, together with the observations previously made on coumarin, vanillin, &c., indicate that apparently inodorous substances may be divided into two groups, namely, those that are truly inodorous under various conditions, and those that are only inodorous under certain particular conditions, but distinctly odorous under other conditions.

C. H. B.

**Action of Salts on Tubifex Rivulorum.** By S. RINGER and H. SAINSBURY (*J. Physiol.*, 16, 1—9).—In a former series of papers, the authors have shown the importance of calcium salts in vital and coagulation processes, and the antagonism existing between calcium and potassium. The present experiments on the fresh-water worm *Tubifex rivulorum* confirm and extend these observations. In tap water, the worms live an indefinite time; in distilled water they are dead and disintegrated within 24 hours. That it is the minute quantities of calcium salts in the river water which prevents this disintegration is shown by adding a calcium salt, in small quantities, to distilled water; in this the worms live a long time. The quantity of calcium salt may, however, be increased enormously without any untoward result, it being very indifferent to the tissues. Calcium salts, both in minimal and massive doses, antagonise the paralysing influence of potassium salts; and whilst a minimal dose of calcium salt has extraordinary powers of inhibiting the action of large quantities of potassium salts, a massive dose of the latter is most easily overcome by a massive dose of a calcium salt.

Sodium contrasts with potassium in the relative feebleness of its action, maintaining its character as an indifferent element.

W. D. H.

**Effect of Hydrogen Cyanide on different Insects.** By R. SCHMIDT (*Exper. Stat. Record*, 5, 593—594; from *Calif. Stat. Rep.*, 1891—92, 233—237).—A number of insects (24 species) were exposed to the action of hydrogen cyanide; it was found that some of the *Coleoptera* were alive after 68 minutes. The effect of the gas and the time of exposure is given in tables.

N. H. M.

## Chemistry of Vegetable Physiology and Agriculture.

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**Effect of Potassium Salts on Nitrification.** By J. DUMONT and J. CROCHETELLE (*Compt. rend.*, 118, 604—606; compare this vol., ii, 116).—In the first experiments, now described, moor soil (containing humus 18·5, lime 0·285, per cent.) was treated with varying amounts of potassium carbonate and sulphate respectively, and kept for 20 days at about 25°. Where no potassium salt was added, the amount of nitric nitrogen formed was 24—25 per million; with carbonate, applied in quantities of 0·1 to 6 per cent., the nitric nitrogen increased to 47 (with 0·1 per cent.), to 65 (with 0·5 per cent.), and to 438 with 4·5 per cent., after which it diminished (to 407 and 375) with 5 and 6 per cent. respectively. The results with potassium sulphate were very irregular, the nitric nitrogen being raised to 50 per million of soil with 0·5 per cent. of sulphate, whilst with the larger quantities (up to 5 per cent.) the amounts varied between 18 and 27 per million.

When, however, calcium carbonate (2·5 per cent.) was given to the soil, in addition to the potassium sulphate, there was a regular and marked increase in the amount of nitric nitrogen produced; for example, with no calcium carbonate or potassium sulphate, 26 parts of nitric nitrogen was produced; with carbonate alone, 30 parts; with carbonate and 0·5 per cent. of sulphate, 75·6 parts; with carbonate and 5 per cent. of sulphate, 189 parts per million. Potassium sulphate is, therefore, rendered efficacious by the presence of calcium carbonate, with which it undergoes decomposition, yielding potassium carbonate. The change is very rapid. Thus, a solution of potassium sulphate filtered through moor soil is almost colourless, but when calcium carbonate is added the solution becomes coloured, especially when the amount of potassium sulphate is increased.

The results are of practical importance in horticulture when soils rich in humus are employed. N. H. M.

**Production of Ammonia in the Soil by Microbes.** By E. MARCHAL (*Bull. Acad. roy. Belg.*, [3], 25, 727—771).—Two lots of soil (250 grams), to which a 10 per cent. of albumin solution (2·5 c.c., containing 0·001 per cent. of ferrous sulphate to prevent coagulation) had been added, were sterilised. The one was kept sterilised, whilst the other was inoculated with a few c.c. of soil extract. After 20 days, the sterilised soil, like the soil at the commencement, contained only traces of ammonia; the inoculated soil contained 34·2 milligrams of ammonia. This confirms the results obtained by Müntz and Coudon (*Abstr.*, 1893, ii, 291), showing that ammonia is produced in soil by microbes and not by a chemical process.

A number of moulds, yeasts, and bacteria were isolated from soils of different kinds, and their action in dilute albumin solutions determined.

As regards bacteria, *Bacillus arborescens*, *B. coli communis* var., *B. figurans*, *B. fluorescens putidus*, and *liquefaciens*, *B. mesentericus vulgaris*, *B. mycoides*, *B. subtilis*, *B. termo*, *B. janthinus*, *Micrococcus albicans*, *Proteus vulgaris*, and *Sarcina lutea*, all produced much ammonia. Most of the other bacteria produced some ammonia; but a few (a non-liquefying *Proteus* and a long, liquefying bacillus) gave no ammonia. The organisms which produced no ammonia developed only slightly. Ammonisation thus differs from nitrification in being brought about by a very large number of microbes.

In many cases, the amount of ammonia formed was determined; it was found that *B. mycoides* was much the most active of the soil organisms.

About 30 moulds were isolated, and their action on albumin investigated, with the result that nearly all were found to produce ammonia. The most active was *Cephalothecium roseum*, which produced 25 milligrams in 50 c.c. in two weeks. It is supposed that in arable soil, where moulds are present only in small amounts, the action of bacteria must predominate, whilst in humus, and soils rich in organic matter, there is no doubt that the moulds take an active part in the mineralisation of organic nitrogen.

The *Bacillus mycoides* (first described by Flüggé as "Erde Bacillus"), being evidently the most important, was further investigated. It occurs constantly in surface soils, and is present in the air and in natural waters. In decomposing albumin, it produces a strongly alkaline solution, due to ammonium carbonate; the carbon is mainly converted into carbonic anhydride, but formic, propionic, and butyric acids are formed in small quantities; the sulphur is oxidised to sulphuric acid. No hydrogen or nitrogen are eliminated in the free state. Slight alkalinity is favourable to the development of the bacillus, but it will develop in solutions containing 0.05 per cent. of sulphuric acid, although not in presence of 0.1 per cent. It will also develop in 0.2 per cent. solutions of potash. A temperature of 30° is the most suitable; below 5° only traces of ammonia are produced, and at 42° none at all. The bacillus will not develop in an atmosphere of hydrogen or carbonic anhydride except in solutions of organic matter and nitrate. Under these conditions, it develops well, the necessary oxygen being obtained from the nitrate, which becomes reduced to nitrite and ammonia. As regards the action in nitrogenous matter other than egg-albumen, the bacillus decomposes other proteids, also leucine, tyrosine, creatine, and asparagine, but not urea; it also fails to develop in solutions of ammonium salts and nitrates, except under the conditions already described. When *B. mycoides* is grown in solutions of albumin and carbohydrates, the solution becomes turbid, shows an acid reaction, and the albumin is precipitated. Acid is formed when glucose, saccharose, lactose, dextrose, and starch are employed, slightly with inuline, but not with gums. The reaction is not definite; under the influence of a zymose secreted by the microbe, the albumin redissolves, and the solution eventually becomes alkaline.

It is concluded that "nitratation" of soil nitrogen is preceded by "ammonisation," followed by "nitrosation," and that the ammonia

producing bacillus can act both as an oxidising and as a reducing agent according to the conditions. N. H. M.

**Vegetable Cell Membranes.** By E. SCHULZE (*Zeit. physiol. Chem.*, 19, 38—69; compare Abstr., 1890, 283; 1892, 907).—The cell membranes, prepared from various seeds by removal of fat and proteid matter by dilute sodium hydroxide, were in confirmation of previous researches found to consist very largely of hemi-celluloses. These, by treatment with dilute mineral acids, yield a pentose (arabinose, or xylose in different cases), and often galactose in addition. The seeds of the blue lupin were those to which special attention was directed; the yield of galactose here is very great. Pentosan, galactan, and mannan appear to be very widely distributed, and act as the mother substances of the respective carbohydrates.

Quantitative analysis gave the following results.

Proteids ( $N \times 6.25$ ) .....	7.25
Organic material free from N.....	89.85
Ash.....	2.90

100.00

Another analytical point made out is the very low percentage of cellulose; in the case of the blue lupin, it is only 3.9 per cent.

E. Gilson (*La Cellule*, 9, 397—410), in a recent investigation of cell membranes in plants, doubts the existence of mannosocellulose, and describes a substance he calls paramannan, which, mixed with cellulose, constitutes mannosocellulose. The author's previous views on the subject are here upheld. Gilson's paramannan is probably not identical with mannosocellulose, but is a hydrate of it.

The paper concludes with a classification of the constituents of cell walls. The author recommends that the term *cellulose* should be restricted to dextroso-cellulose, that is, to cellulose which yields dextrose, and the other celluloses should be called *hemi-celluloses*. In addition to these, *amyloid* and *mucus-yielding* substances are present. Reiss has designated mannose (seminose) *reserve cellulose*, that is, it is dissolved and used in the growth of the seedling; this term, however, must be extended to include part at least of the hemi-celluloses.

W. D. H.

**The Taking Up of Calcium Chloride by Plants.** By E. JENSCH (*Zett. angew. Chem.*, 1894, 111—112).—Raspberries and strawberries growing round the edges of puddles below the Schwarzerger smelting works, in the Erzgebirge, were noticed to be generally of an unusually large size. The plants growing on the drier places generally had badly shaped fruit covered with a white substance, whilst the fruit of the plants nearer the water was very large and brightly coloured. All the fruit differed from that of more distant plants in being more quickly perishable. The fruit and stems, especially of the raspberries, tasted strongly of calcium chloride; the leaves only slightly. The origin of the calcium chloride was an accident which had taken place six months previously, when a quantity of a solution of calcium and copper chlorides flowed out of

an extracting drum over the ground. The following analyses are given.

	Dry matter.	Ash.	Cl.
Healthy raspberries.....	17.41	0.88	—
Diseased „ from dry ground	11.52	1.96	0.20
„ „ „ damp „	8.35	1.52	0.13
Strawberries, healthy .....	12.03	0.72	—
„ „ diseased .....	7.16	1.24	0.04

All the ashes contained traces of copper.

N. H. M.

## Analytical Chemistry.

**Modified Litre Flask.** By W. B. GILES (*Chem. News*, 69, 99—100).—In the neck of the flask above the litre mark, the author provides an enlargement, and a second mark indicates an additional volume of 100 c.c. When preparing a solution, 1100 c.c. is allowed for, and the solution made rather too strong, the 100 c.c. in excess serving for the necessary standardising tests, and, as exactly a litre remains, the final adjustments to the desired strength are much facilitated.

D. A. L.

**Use of Sodium Hydrogen Tartrate in Alkalimetry.** By A. BORNTRÄGER (*Zeit. angew. Chem.*, 1894, 54—55).—The author, in reply to several critics, states as his opinion that sodium hydrogen tartrate when *pure* is the most suitable substance for standardising normal alkalis.

L. DE K.

**Detection of Free Mineral Acids in presence of Organic Acids.** By E. NICKEL (*Chem. Zeit.*, 17, 1670).—The author recommends the following process for the detection of, say, hydrochloric acid in vinegar:—The sample is mixed with a large quantity of phloroglucinol, and then boiled for a while with a piece of pine wood or bamboo. After further contact for about 12 hours, the wood will assume the well-known characteristic colour if any free mineral acid be present.

L. DE K.

**Estimation of Iodine in Presence of Bromine and Chlorine.** By M. GRÜGER (*Zeit. angew. Chem.*, 1894, 52—54).—The process is based on the fact that alkali iodides are converted into iodates by the action of potassium permanganate, whilst bromides or chlorides are not affected.

The solution, which should contain no ammonia, is heated on a boiling water bath, and a 4 per cent. solution of potassium permanganate is added until the supernatant liquid turns decidedly red. The excess of permanganate is then reduced by adding a few drops of alcohol. The liquid is filtered and the precipitate thoroughly washed



by decantation. The author recommends working on a small quantity of the iodide mixture, so as to have only about 0.05 gram of iodine present; otherwise there is too much precipitate, and the washing takes a very long time. The filtrate, after cooling, is mixed with 0.5 gram of potassium iodide, acidified with hydrochloric acid, and the liberated iodine is then titrated with sodium thiosulphate. One-sixth part of the iodine found was originally present in the sample. To estimate iodine in the crude article, 0.5–1 gram is dissolved in its own weight of sodium hydroxide contained in a little water. The solution is made up to 250 c.c., and 25 c.c. is pipetted off and treated with permanganate as directed. The test-analyses are very satisfactory.

L. DE K.

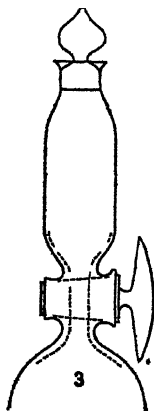
**Detection of Iodates in Alkali Iodides.** By M. SPICA (*Gazzetta*, 24, i, 91–95; compare Robineau and Rollin, *Abstr.*, 1893, ii, 183).—Small quantities of iodate in potassium iodide, employed for medicinal purposes, may be detected by taking advantage of the fact that barium iodate requires 1736 parts of water at 15° for its solution. Any precipitate deposited on adding barium chloride to a solution of potassium iodide may be due to the presence of a carbonate, iodate, or sulphate. If the precipitate consists of barium iodate, it should be soluble in hot concentrated hydrochloric acid, and should again separate on diluting with water. 0.002 gram of potassium iodate in 100 grams of potassium iodide can be detected by this test.

W. J. P.

**Estimation of Ammonia in Presence of Sulphides or Cyanides.** By E. HENRY (*Bull. Soc. Chim.*, [3], 9, 1018).—In the usual method of distillation with alkali, appreciable quantities of hydrogen sulphide or cyanide are liable to pass over when sulphides or cyanides are present. These should, therefore, be precipitated with basic lead acetate before distilling.

JN. W.

**Estimation of Nitric acid with the Nitrometer.** By E. HENRY (*Bull. Soc. Chim.*, [3], 11, 24–27).—In the ordinary forms of nitro-



meter suitable for the analysis of solids, the funnel is usually ground into the main tube, and is liable, therefore, on the one hand, to be blown out by the evolved gas, or, on the other hand, to be crushed by the fingers of the operator. This defect is remedied in the instrument depicted. The funnel forms an extension of the reaction tube, and the solid is dissolved in it, instead of in the latter. The upper end, for this purpose, is stoppered, and the tap at the lower end provided with a channel of unusually large diameter. When the substance is completely dissolved, the solution is washed into the mercury tube with sulphuric acid in the usual way. The reaction is best carried out at a low pressure to diminish the error due to dissolution of nitric oxide in the acid. JN. W.

**Detection of Nitrites in Urine.** By A. JOLLES (*Zeit. anal. Chem.*, 32, 762—766).—In consequence of the absorption of iodine by both the normal and pathological constituents of urine, the usual test for nitrites with potassium iodine and starch paste is not sufficiently sensitive, especially in view of the poisonous effect of the introduction of mere traces of nitrites into the blood. The lower limit of the test is not constant, but in a specimen of albuminous urine experimented with, no smaller quantity than 0.003 gram of  $N_2O_3$  in 10 c.c. could be detected. The reaction with sulphanilic acid and  $\alpha$ -naphthylamine will detect 0.000032 gram of  $N_2O_3$  in 100 c.c. The urine must be decolorised by warming to  $40^\circ$  and shaking with a pinch of blood charcoal. 100 c.c. is then placed in a cylinder with a good ground stopper, acidified with sulphuric acid, then treated with 1 c.c. of sulphanilic acid, and, after a few minutes, with 1 c.c. of  $\alpha$ -naphthylamine, and the cylinder stoppered air-tight. With the above quantity of nitrite, the rose-red colour requires 25 minutes for development.

Schüffer's reaction (see Deventer, *Abstr.*, 1893, ii, 298) is almost equally sensitive, and can be applied to as little as 3 c.c. of the decolorised urine. This quantity is mixed in a test tube with an equal volume of acetic acid (1 : 10) and then 2, or at most 3, drops of potassium ferrocyanide (1 : 20). In presence of a nitrite, a yellow colour results from the oxidation of the ferrocyanide to ferricyanide. For highly dilute solutions of nitrites, the author is unable to confirm Deventer's quantitative results, and can suggest no better means for quantitative estimation than Trommsdorff's zinc iodide-starch method), applied to the decolorised urine, and executed as rapidly as possible. The most suitable quantity of the Trommsdorff solution to be used must be ascertained in each case as it is not constant. M. J. S.

**Rapid Method for the Estimation of Phosphorus in Titaniferous Iron Ores.** By C. BASKERVILLE (*J. Anal. and Appl. Chem.*, 7, 194—196).—2 grams of dried and finely-powdered ore is thoroughly mixed with 20 grams of a mixture of 10 parts of sodium carbonate and 1 part of potassium nitrate and fused in a spacious platinum crucible. After cooling, the mass is repeatedly boiled with water, and the liquid, measuring about 300 c.c., is filtered, the insoluble

matter being well washed with hot water; 25 c.c. of solution of ferric chloride, containing about 0.1 gram of iron is added; the solution is acidified with hydrochloric acid, boiled, and precipitated with ammonia. After collecting and washing, the iron precipitate is dissolved in 40 c.c. of hot nitric acid (sp. gr. 1.43), 25 c.c. of strong ammonia is added, the liquid heated or cooled to 85°, and mixed with 30 c.c. of molybdate solution. After well shaking for five minutes, the molybdate precipitate is collected, and finally titrated according to the Manby-Handy method. L. DE K.

**Estimation of Phosphoric acid by titrating the Molybdic Precipitate.** By H. PRIBERION (*Chem. Centr.*, 1894, 1, 105; from *J. Amer. Chem. Soc.*, 15, 382—395).—1 gram of the phosphate is dissolved in nitric acid and diluted with water to 250 c.c.; 25 c.c. is neutralised with ammonia, and then mixed with 5 c.c. of nitric acid (sp. gr. 1.4); 10 c.c. of a saturated solution of ammonium nitrate and 20 c.c. of water is next added, and the whole heated to boiling. An aqueous solution of ammonium molybdate (90 grams per litre) is now added in portions of 5 c.c. as long as a precipitate is produced. This is washed by decantation, a filter being also used, and then dissolved in a known volume of standard alkali. After adding phenolphthalein, the excess of alkali is titrated back with standard acid.

If 1 c.c. of the alkali is to correspond with 0.001 gram of phosphoric anhydride, its strength should be 0.3265—normal.

L. DE K.

**Decomposing Silicates by Concentrated Hydrochloric acid under Pressure.** By P. JANNASCH (*Zeit. anorg. Chem.*, 6, 72).—The author claims priority for this method, which is effected in a platinum cylinder contained in a glass tube, the pressure on which is equalised by enclosing it in a Mannesmann tube containing ether.

A. G. B.

**Solvent Action of Tartrates on Metallic Hydroxides.** By H. N. WARREN (*Chem. News*, 69, 125).—The author points out that the solvent action of normal tartrates is not restricted to the hydroxides and carbonates of ferric, cupric, and antimoniacal origin, but extends also to the ferrous, zinc, manganese, nickel, cobalt, chromium, aluminium, barium, strontium, magnesium, calcium, bismuth, and tin precipitates. As regards the last two metals, this point appears to be frequently overlooked by analysts; cadmium carbonate is practically insoluble in this medium, and may therefore be separated from the copper compound by digesting such a mixture with a normal tartrate.

D. A. L.

**Electrolytic Separations.** By E. F. SMITH (*Zeit. anorg. Chem.*, 6, 40—42 and 43—44).—It is pointed out that Freudenberg's observations on this subject (*Abstr.*, 1893, ii, 506) are not new, but in most cases confirm the work of Smith and his collaborators.

The second paper is a continuation of a discussion with Classen.

A. G. B.

**Electrolytic estimation of Copper in Invert-Sugar Determinations.** By B. B. ROSS (*J. Anal. and Appl. Chem.*, 7, 83—86).—The author has modified Formanek's process and operates as follows.

The precipitation of the cuprous oxide is effected in a beaker, and the precipitate is at once brought upon an asbestos filter in an ordinary funnel, and washed with hot water. The precipitate need not be completely transferred to the filter, which is replaced in the beaker, and the funnel is then rinsed with weak nitric acid containing 4 c.c. of acid (sp. gr. 1.42) to 100 c.c. of solution. The acid is added to the contents of the beaker until there is about 200 c.c. of liquid, and, after the platinum electrodes are introduced, connection is made with a battery giving a current equivalent to 0.5–0.7 c.c. of electrolytic gas per minute. The anode employed is a flat spiral of platinum wire of Luckow's pattern, and rests on the bottom of the beaker, whilst a vertically suspended platinum cylinder of the usual form receives the deposit of copper. It is not necessary to wait until the cuprous oxide has completely dissolved before closing the circuit.

The test analyses show the remarkable accuracy of the method.

L. DE K.

**Rapid Analysis of Blast Furnace Slag.** By O. TEXTOR (*J. Anal. and Appl. Chem.*, 7, 257–262).—The author estimates the silica and alumina in the usual manner by evaporating quickly 0.5 gram of the slag with hydrochloric acid, &c. Whilst this is going on, 1.325 grams of the slag is dissolved in dilute hydrochloric acid, oxidised with a few drops of nitric acid, rendered alkaline with ammonia, and diluted to 530 c.c. After filtering, 200 c.c. (= 0.5 gram slag) is used for the estimation of the calcium by the permanganate process. 250 c.c. is mixed with excess of ammonium oxalate diluted up to 300 c.c., and filtered. 240 c.c. of the filtrate (0.5 gram slag) is precipitated with ammonia and sodium phosphate, and the precipitated ammonium magnesium phosphate washed with dilute ammonia. To save time, the precipitates of the silica, alumina, and magnesium phosphate are washed with the aid of the filter pump, and burnt moist. The alumina may contain traces of iron and the magnesia traces of manganese, but these do not as a rule appreciably affect the results. Sulphur existing as a sulphide may be estimated by treating 0.5 gram of the slag with standard iodine in presence of hydrochloric acid. The excess of iodine is then titrated in the usual manner.

The author does not pretend to great accuracy, but claims to make satisfactory analyses of several samples within a couple of hours.

L. DE K.

**Separation of Ferric, Manganous, Calcium, and Magnesium Phosphates.** By R. SEELIGER (*Chem. Centr.*, 1894, i, 107–108; from *Pharm. Centr.-Halle* [2], 14, 685–687).—About 0.3 gram of the mixed phosphates is fused in a platinum crucible with 10 times its bulk of an intimate mixture of sodium carbonate, potassium nitrate, and silica, first over a Bunsen burner, then over a blow-pipe. After cooling, the mass is lixiviated with hot water and any potassium manganate is reduced by passing a few bubbles of hydrogen sulphide. The insoluble matter is dissolved in hydrochloric acid, and, after adding a slight excess of sodium carbonate, mixed with the main liquid. After boiling, the mixture is left for 12 hours, when the bases will have been precipitated as carbonates and

silicates, the phosphoric acid being contained in the alkaline liquid, from which it may be precipitated by magnesium mixture after removing the silica.

The bases are dissolved in hydrochloric acid, the silica rendered insoluble, and the hydrochloric acid filtrate neutralised with ammonia; the iron and manganese are then precipitated by boiling with sodium acetate and bromine. The filtrate containing the lime and magnesia is first evaporated to a small bulk, in order to remove any remaining traces of manganese, and then treated as usual. The iron is finally separated from the manganese by the acetate method.

L. DE K.

**Separation of Nickel and Cobalt in Steel Analyses.** By H. V. JÜPTNER (*Chem. Centr.*, 1894, i, 229—230; from *Österr. Zeit. Berg. Hutt.*, 41, 616).—Fresenius has proved that small quantities of ferric oxide may be completely separated from cobalt and nickel oxides by adding to the hot solution ammonium chloride and excess of ammonia. The precipitate must, however, be freed from impurities by redissolving in hydrochloric acid and reprecipitating with ammonia for a second and third time. The nickel and cobalt are then precipitated by ammonium sulphide, the mixture being finally neutralised with acetic acid. The author fully confirms the accuracy of the method, which gives good results even if the iron exceeds the nickel and cobalt by 200 to 1. If manganese be present, a slight excess of acetic acid should be added. The process also works in presence of alumina.

L. DE K.

**Separation of Thorium from the Rare Earths of the Cerium and Yttrium Groups by means of Potassium Nitride.** By L. M. DENNIS and F. L. KORTRIGHT (*Amer. Chem. J.*, 16, 79—83).—The authors find that when potassium nitride,  $\text{KN}_3$ , is added to a neutral or nearly neutral solution containing thorium and its allied earth metals; the thorium is precipitated as hydroxide (hydrogen nitride being liberated), whilst the other earth metals remain in solution. The precipitated thorium hydroxide is free from any appreciable quantity of cerium or other earth metals. L. T. T.

**Estimation of Organic Matter in Potable Water by means of Permanganate.** By P. E. ALFSSANDER (*L'Orosi*, 16, 397—400).—Kubel's process for the determination of organic matter in water consists in boiling the water for some time with dilute sulphuric acid, and then titrating the boiling liquid with permanganate; the quantity of organic matter present is taken to be five times the weight of potassium permanganate which the water decolorises.

The author proposes to use a standard solution of potassium permanganate containing 0.200 gram per litre for the titration; it is made up by dissolving the necessary quantity of permanganate in a litre of distilled water. 100 c.c. of the water is boiled for five minutes with 10 c.c. of dilute sulphuric acid, and the standard permanganate is added until the colour is no longer discharged. It is then boiled again for 6—7 minutes, and if the colour disappears, more permanganate is added as before. The number of c.c. of this solution

decolorised by a litre of the water gives directly the number of centigrams of organic matter per litre. A standard solution, prepared by dissolving 0.400 gram of pure crystallised oxalic acid in a litre of water, may be conveniently employed to determine the excess of permanganate added to the water. W. J. P.

**Simultaneous Estimation of Carbon, Hydrogen, and Nitrogen.** By H. MALFATTI (*Zeit. anal. Chem.*, 32, 754—761).—The method described is a modification of that of Janusasch and V. Meyer, but is not yet perfected, the results being still somewhat deficient in accuracy. Two tubes, the combustion tube and the reduction tube, are laid side by side in sheet-iron troughs in a Glaser's combustion furnace. One end of the combustion tube is connected with an apparatus for supplying oxygen, consisting of a hard glass tube containing strongly dried potassium chlorate and cupric oxide, a Y-tube containing 50 per cent. potash solution, and serving both as a counter and as a pressure gauge by having its lower limb connected with a mercury reservoir; a U-tube containing soda lime, calcium chloride, and large plugs of cotton wool, and then a good glass stopcock. The combustion tube contains in order, oxidised copper spirals, the boat with the substance, 16 cm. of reduced copper, obtained by wrapping fine-grained scale copper oxide in copper gauze, and reducing by methylic alcohol, a short plug of silver gauze, and lastly 25 cm. of scale copper oxide. Next in order follow the usual absorption vessels, but between the calcium chloride tube and the potash bulbs there is inserted a Y-tube, whose lower limb is connected with a mercury reservoir by thick walled caoutchouc tubing a meter in length. Following the Liebig's bulbs comes an arrangement constructed from three Y-tubes and a mercury reservoir, by the adjustment of which communication between the combustion and reduction tubes may either be shut off while the air is expelled from the former by oxygen and from the latter by carbonic anhydride, or else the two tubes may be put in communication, and the carbonic anhydride supply be shut off. At the other end of the reduction tube, which is filled with scale copper oxide, all of which except the last 10 cm. is reduced by hydrogen, is attached a Zulkowsky-Ludwig apparatus to receive and measure the nitrogen.

After expelling the air from the combustion tube by oxygen, and from the reduction tube by carbonic anhydride, while heat is applied to the copper oxide, the stopcock, and a clamp between the manometer and the potash bulbs are both closed, and by heating the copper spirals the oxygen in the combustion tube is absorbed. The substance is then heated, and when by its combustion a small positive internal pressure is indicated by the manometer the clamp is opened and the gases allowed to bubble through the Liebig bulbs, the nitrogen passing on into the reduction tube. Oxygen is again admitted, and continued until the substance is completely burnt. During this stage the copper spirals in the combustion tube must be cooled so that the oxygen may sweep all the other gases out of the tube. All the oxygen which passes into the reduction tube is there retained by the copper, and when the cessation of the escape of gas into the Zul

kowsky apparatus indicates that nothing but pure oxygen is passing from one tube to the other, the communication between them is closed, and the remaining nitrogen expelled by carbonic anhydride. The whole combustion takes about an hour. Blank experiments must be made, since a small volume of uncondensable gas is always obtained, even when nitrogen is not present. On the other hand, traces of the nitrogen oxides escape reduction, and being absorbed in the potash bulbs raise the carbon results. A further error of excess appears to be due to the adhesion of traces of carbon and hydrogen to the porous copper obtained by reduction with methylic alcohol.

M. J. S.

**Estimation of the Nitrogen in Benzene Pyridine and Quinoline Derivatives by Kjeldahl's Method.** By M. KÄÜGER (*Ber.*, 27, 609—613).—The substance (0.2—0.8 gram) is dissolved in strong sulphuric acid (20 c.c.), contained in a round bottomed flask, heat being applied if necessary. To the cooled solution, potassium dichromate is added, 0.5 gram at a time, to the extent of 0.5 gram more than the amount theoretically necessary for the oxidation. After any evolution of gas has ceased, the flask is placed in a cold water bath, which is then heated to boiling. The flask is kept there until no more gas is evolved, and is then heated on wire gauze with a small flame until the evolution of gas ceases, and the colour of the mixture is a pure green; this indicates the completion of the oxidation, which occupies only 15—30 minutes in all. The ammonia in the mixture is now estimated in the usual way. Good results are obtained with compounds containing no nitrogen, that is directly joined to oxygen or to another nitrogen atom; substances containing such nitrogen have yet to be experimented with. The advantages of this over the other modifications of Kjeldahl's method are (1) the rapidity of the oxidation, and (2) the means of telling when the oxidation is complete.

C. F. B.

**Apparatus for the Rapid Estimation of Combustible Gases.** By G. G. POND (*Ber.*, 27, 692—696).—This apparatus is due to Shaw (Philadelphia). It consists of a pump provided with two cylinders, one of fixed, the other of variable, volume, by means of which mixtures of air or any gas which has to be examined, with a combustible gas can be rapidly and accurately made, so that the resulting mixture contains a known percentage of the added combustible gas. This mixture then passes into a chamber in which it meets with a flame, and, if it explodes, the force of the explosion moves a piston which sounds a bell. In order to rapidly determine the percentage of combustible gas in a sample of air from a coal mine, for example, a mixture of pure air with coal-gas is made which will just explode and sound the bell of the apparatus. The sample of gas is then substituted for the air, and the amount of coal-gas added diminished until the limit of explosibility is again reached. The difference between the amounts of coal-gas added to reach this limit in the two experiments represents the amount of combustible gas originally present in the sample tested. It is claimed that the apparatus is

sensitive to 0.1 per cent. of combustible gas. The apparatus is also of value for the rapid and exact preparation of mixtures containing known amounts of combustible gas, and may thus be applied to the testing of Davy lamps. A. H.

**Estimation of Oil of Turpentine in Alcohol.** by J. PERL (*Chem. Zeit.*, 17, 1851).—Alcohol containing turpentine will stand more or less dilution with water before a turbidity is produced. The more turpentine is present, the less will be the amount of water required. On this fact, the author bases his process for a quantitative estimation of turpentine in denatured spirits. 5 c.c. of the sample is put into a test-glass, and water is added from a burette until a permanent turbidity is produced. 5 c.c. of a 0.5 per cent. solution of turpentine in spirit of the same alcoholic strength as the sample is put into another test-glass, and also titrated. The mixture which consumes most water is the poorest in turpentine, and the author found that 1.1 c.c. of difference in water is equivalent to 0.25 per cent. of turpentine. The author also found that the turpentine cannot be removed by fractional distillation over lime. L. DE K.

**Estimation of Alcohol in Wines.** By A. BORNTRAEGER (*Zeit. angew. Chem.*, 1894, 108—110).—The author dilutes 100 c.c. of the sample with an equal bulk of water, distils off two-thirds or more, dilutes the distillate to exactly 100 c.c., and takes its specific gravity at 15.5°.

Unless the sample contains more than 0.5 per cent. of volatile acidity, which is rarely the case, it is not necessary to neutralise before distillation. L. DE K.

**Estimation of Phenol.** By L. ZIMMERMANN (*J. Pharm.*, [5], 29, 105—110).—A modification of Chandelot's method. The aqueous phenol is added to aqueous potassium hypobromite until the latter ceases to discolour starch paper impregnated with potassium iodide and sodium carbonate, the titre of the hypobromite having been found by a similar experiment with a solution of pure phenol of known strength.

If the dilution of the phenol is not greater than 250 c.c. per gram., the result may be calculated at once from the volume used, but if greater than this, a correction is necessary on account of the lack of sensitiveness of the indicator. This correction is proportional to the square of the dilution, so that its values lie on a rectangular parabola,  $y = ax^2$ , when plotted against it. The value of the constant  $a$ , corresponding with 20 c.c. of Chandelot's hypobromite, is 0.00484.

The approximate dilution of the phenol solution of which it is desired to ascertain the strength having been ascertained by titration, the value of the correction  $y$  is found from the equation and added to the number of c.c. required to saturate the hypobromite, and the actual dilution then calculated. The numbers quoted show very fair agreement. Tables are given to facilitate the correction.

JM. W.



**Solubility of Lead Salts in Sugar Solutions: Estimation of Sugar in Sweet Wines.** By J. STERN and P. HIRSCH (*Zeit. angew. Chem.*, 1894, 116—117).—The authors have found that, on adding sodium carbonate to a wine containing excess of lead acetate, the precipitated lead carbonate more or less redissolves in excess of the reagent, and that this is due solely to the presence of levulose.

The excess of lead is, however, completely removed by a current of carbonic anhydride.  
L. DE K.

**Gravimetric Estimation of Pentaglucooses.** By E. R. FLINT (*J. Anal. and Appl. Chem.*, 7, 190—194).—The author claims the priority as regards the gravimetric estimation of furfuraldehyde with phenylhydrazine lately proposed by Chalmot. The majority of articles to be tested (plants and fodder articles) contain more or less of glucosides, which, on distillation with hydrochloric acid, yield levulinic acid, acetone, and similar compounds; these pass into the distillate, and would count as furfuraldehyde when the volumetric process is employed. But as these compounds do not give a precipitate with phenylhydrazine, at least in weak solutions, the accuracy of the gravimetric estimation is not influenced by their presence.

The factors for the conversion of the hydrazone into furfuraldehyde, arabinose, xylose, and pentose are respectively:  $\times 0.538$ ;  $\times 1.229 + (0.0177)$ ;  $\times 1.031 - (0.001)$ ;  $\times 1.13 + (0.0083)$ . Pentose may be calculated to pentosan by multiplying by 0.88.

L. DE K.

**Estimation of Pentosans.** By E. HOTTER (*Chem. Zeit.*, 17, 1743—1745).—5 grams of the substance containing the pentosan—bran for instance—is distilled with hydrochloric acid of 1.06 sp. gr. until the distillate no longer shows the furfuraldehyde reaction with aniline acetate. The distillate is diluted with hydrochloric acid up to a definite bulk, say 400—500 c.c. and 20—30 c.c., and after the addition of some pyrogallol, is heated in a sealed tube for two hours at 100—110°. The precipitate which forms is collected on a tared filter, washed, and dried at 103°. Its weight, divided by 1.974, gives the amount of furfuraldehyde.

100 parts of pentosan should yield 64 parts of furfuraldehyde, but, owing to secondary reactions, the amount rarely exceeds 50 per cent.  
L. DE K.

**Estimation of Alkalinity and Acidity of Urine.** By E. FREUND and G. TOEPFER (*Zeit. physiol. Chem.*, 19, 84—103).—The determination of the reaction of urine is complicated by the presence of various salts, some of which have an acid and others an alkaline reaction. In order to overcome this difficulty, a number of indicators were examined, and it was found that some are differently affected by free acids and alkalis, as distinguished from acid and alkaline salts. The following table gives the chief results.

Reagent.	Colour produced in					
	Alizarin.	Alizarin-blue.	Methyl-orange.	Poirier's-blue.	Brilliant-crocein.	Phenolphthalein.
Free acid. . . .	Lemon-yellow	Orange	Red	Blue	Red	Colourless
Monosodium phosphate	Orange	Orange	Orange	Blue	Red	Colourless
Disodium phosphate	Red	Yellow-green	Yellow	Blue	Red	Pink
Sodium hydrogen carbonate	Red	Yellow-green	Yellow	Blue	Red	Colourless
Sodium carbonate	Violet	Dark green	Bright yellow	Violet	Brown-red	Red
Trisodium phosphate	Violet	Dark green	Bright yellow	Violet	Brown-red	Red
Free alkali . .	Deep violet	Dark green	Bright yellow	Red	Brown	Deep red

The next table shows how the indicators may be used quantitatively with solutions.

Solutions.	Alkalinity.		Acidity.		
	Quantity of decinormal HCl used in c.c.		Quantity of decinormal NaOH in c.c.		
	To decolorise phenolphthalein.	To turn alizarin yellow.	To turn phenolphthalein dark red.	To turn alizarin violet.	To turn Poirier's-blue red.
10 c.c. of 1 per cent. monosodium phosphate	—	0.05	8.35 = 0.98 per cent.	8.3 = 1 per cent.	16.6 = 1 per cent.
10 c.c. of 1 per cent. disodium phosphate	0.1	6.9 = 0.99 per cent.	0.1	0.1	6.95 = 0.99 per cent.
10 c.c. of 1 per cent. trisodium phosphate	6.3 = 1.05 per cent.	12.3 = 1 per cent.	—	—	0.05
10 c.c. of 1 per cent. sodium hydrogen carbonate	0.1	11.6 = 0.99 per cent.	2.0	2.0	11.8 = 1 per cent.
10 c.c. of 1 per cent. sodium carbonate	9.4 = 1 per cent.	18.3 = 0.988 per cent.	—	—	0.1

Sodium carbonate thus gives a measure of acidity, and trisodium phosphate of alkalinity. Disodium phosphate and sodium hydrogen carbonate have an acidity to one reagent equal to their alkalinity to another.

Mixtures of various salts were next subjected to titration; by using different indicators, a very accurate estimation of the proportions present was obtained.

Three examples of the method as applied to urine are given. The headings of the table being the same as in the last, the results obtained were:—

1. 10 c.c. of afternoon urine .....	—	10·1	0·6	0·6	12·65
2. 10 c.c. of urine before meal .....	—	8·7	1·4	1·4	7·4
3. 10 c.c. of urine after meal .....	—	7·2	1·2	1·4	10·8

The first specimen of urine gave an alkaline reaction to litmus paper, but, nevertheless, contained a high amount of acid salts, whereas the second and third specimens, which were from the same individual, were acid to litmus paper, but still contained alkaline salts. It will be further noticed in these two specimens that the values for the acid salts were unchanged by the meal, but that the alkaline salts were nearly doubled.

W. D. H.

**Estimation of the Acidity of Gastric Juice.** By G. TOEPFER (*Zeit. physiol. Chem.*, 19, 104—122).—The object of the present research was to furnish the clinical observer with a ready method by which titration could be employed to indicate not only the total acidity of the contents of the stomach but also the proportion of the various acids to which this is due. The plan of the investigation resembles that described in the preceding abstract. A large number of indicators were tried, first with acids, then with mixtures of these with albumin, and, finally, with artificial digestive mixtures, and also with the contents of the stomach. The following method was adopted. The reagents necessary are, (1) a decinormal solution of sodium hydroxide; (2) a 1 per cent. alcoholic solution of phenolphthaleïn; (3) a 1 per cent. aqueous solution of sodium alizarinsulphonate; and (4) a 0·5 per cent. alcoholic solution of dimethylamidoazobenzene.

5 to 10 c.c. of the gastric mixture is placed in each of three beakers; to the first, two drops of phenolphthaleïn solution is added, and the sodium hydroxide run in from a burette until a quite dark-red is obtained, not deepened, by further addition of alkali.

To the second portion, three or four drops of the alizarin solution is added, and titration again performed, until the first appearance of a pure violet tint (similar to that given by 5 c.c. of 1 per cent. sodium carbonate with the four drops of the alizarin solution) indicates the end reaction.

To the third portion, three or four drops of the dimethylamidoazobenzene solution are added, and titration performed until the last trace of red has disappeared, and is replaced by yellow.

The third titration gives the value of the free hydrochloric acid.

The difference between the first and second titration gives the value of the loosely combined hydrochloric acid. The second titration gives the total acidity. The total acidity *minus* the free and loosely combined hydrochloric acid gives the amount of acidity due to other factors, especially organic acids and acid salts. W. D. H.

**Preservation of Milk for Estimation of Fat.** By M. WEIBULL (*Exper. Stat. Record.*, 5, 536—537; from *Svensk. kemisk. Tidskr.*, 1893).—Potassium permanganate (60 to 100 milligrams) is added to about 20 c.c. of milk which will then keep for several months at 64—72° F. Sufficient permanganate is added to produce a dark-brown colour, the milk being shaken until it is completely dissolved; the colour disappears in a few days when more permanganate is added. Comparative analyses with fresh milk and with milk kept 6 to 56 days, gave results in which the greatest difference was 0.1 per cent., whilst in eight out of eleven cases the difference was 0.05 per cent. or less.

N. H. M.

**Estimation of Fat in Bread.** By M. WEIBULL (*Exper. Stat. Record.*, 5, 520; from *Svensk. kemisk. Tidskr.*, 1892, No. 5).—Direct extraction of bread with ether, however long continued, gives too low results, owing to the fat being enclosed by the starch and dextrin. The results were lower than those obtained from the flour from which the bread was made. The following method is given. The dry powdered bread (1—3 grams) is boiled for an hour with water (15—20 c.c.) containing 10 drops of dilute sulphuric acid, stirring occasionally. The solution is then neutralised with marble free from fat, and the thick solution transferred to a fat-free filter paper, the beaker being wiped out with absorbent cotton. The paper and cotton are dried at 100° and extracted with dry ether for 10 hours.

Comparative estimations of the fat in bread and in the flour from which it was made gave perfectly concordant results by this method.

N. H. M.

**Estimation of Asparagine.** By J. LEWINSKY (*Chem. Centr.*, 1894, i, 53—54).—See this vol. ii, 216.

**Estimation of Emetine in Radix Ipecacuanhæ.** By C. C. KELLER (*Chem. Centr.*, 1894, i, 236—238; from *Schweiz. Woch. Pharm.*, 31, 473—477).—*1st method.* 12 grams of the powdered air-dried drug is extracted in a suitable apparatus with ether to remove the fat. It is then transferred to a counterpoised 200 c.c. flask and mixed with more ether, so that the weight of the latter shall be 90 grams. 30 grams of chloroform is then added, and after five minutes 10 c.c. of a 10 per cent. ammonia solution, and the whole shaken vigorously for half an hour. 10 c.c. of water is now introduced, and after again shaking for a few minutes, 100 c.c. of the clear solution is poured off; the ether and chloroform are removed by distillation, the residue is washed a few times with a small quantity of ether, then dried for 15 minutes in the water bath, weighed, and

titrated with N/10 hydrochloric acid, 1 c.c. of which equals 0.0254 gram of emetine.

*2nd method.* 12 grams of the powder is put into a dry bottle and repeatedly shaken with 90 grams of ether and 30 grams of chloroform. After 5 minutes, 10 c.c. of ammonia is added, and after half an hour 10 c.c. of water; 100 c.c. of the clear liquid is then poured off and shaken in a separating funnel three times in succession with 25, 15, and 10 c.c. of 1 per cent. hydrochloric acid. The acid layer is then made alkaline with ammonia and agitated twice with 50 c.c. of a mixture of 3 parts of chloroform and 2 parts of ether. The solvent is removed by distillation and the residue finally titrated as before.

L. DE K.

**Modification of Grandeau's Method for the Estimation of Humus.** By H. A. HUSTON and W. F. McBRIDE (*Exper. Stat. Record*, 5, 559—560; from *Indiana Stat. Bull.*, No. 46, 67—79).—When investigating the black soils of Indiana, it was found that in some cases the extraction with ammonia by Grandeau's method required over a week. There was also a difficulty of repeating experiments under the same conditions since the percolation through duplicate samples of the same soil was not uniform as to rate. In the modified method, a definite amount of soil is kept in contact with a definite volume of ammonia for a fixed time. The soil, after being washed as usual with acid and water, is washed into a 500 c.c. stoppered cylinder with 500 c.c. of ammonia. After being shaken, the cylinder is kept for 24 hours in an inclined position (without letting the liquid touch the stopper), and for 12 hours in an upright position, to allow the soil to settle before taking out an aliquot part of the solution. The results were much higher than those obtained by the original method, but soils extracted by the old method give further quantities of humus when extracted a second time, making the results nearly the same when 2 per cent. ammonia is employed.

In soils not peaty, the strength of the ammonia makes practically no difference in the results, whilst with peaty soils comparatively little difference is found when the strength is 2 per cent. or more. The adoption of a standard temperature for the digestion is recommended.

The results are much more concordant than those obtained by the original method.

The large number of phosphoric acid and potash determinations made in the ash of the extracted humus did not show any relation between the amounts of humus and of phosphoric acid and potash respectively. There is no evidence to show that either substance is associated with humus before its extraction.

N. H. M.

## General and Physical Chemistry.

**Molecular Refraction.** By H. JAHN and G. MÖLLER (*Zeit. physikal. Chem.*, 13, 385—397).—A continuation of the researches of Landolt and Jahn (*Abstr.*, 1893, ii, 57). The method used was the determination of the dielectric constant, this being effected by comparison with that of metaxylene. The refraction also was observed for the  $H_\alpha$ ,  $H_\beta$ ,  $H_\gamma$ , and  $Na$  lines, and the constants calculated in Cauchy's formula,  $\mu = A + \frac{B}{\lambda^2}$ . In the substances observed, the values for  $\sqrt{\kappa}$  ( $\kappa$  = dielectric constant) and  $A$  did not agree, the former being in all cases too high, *i.e.*, the dispersion is anomalous.

	$\sqrt{\kappa}$ .	$A$ .
Amylic chloride .....	2.5284	1.3987
Tertiary amylic chloride.....	3.0737	1.3956
Amylic bromide.....	2.4853	1.4317
Ethylenic chloride.....	3.259	1.4342
Ethylenic bromide.....	2.1940	1.5207
Bromobenzene.....	2.3274	1.5339
Chlorobenzene.....	2.3504	1.5003
Benzyl chloride.....	2.6291	1.5146
Chlorotoluene.....	2.3064	1.5003
Amylenic bromide.....	2.3648	1.4920

The dispersion-free molecular refraction is also calculated by the formula  $M \frac{\kappa - 1}{\kappa + 2} \cdot \frac{1}{d}$ . As thus determined, the chloro- and bromo- compounds of univalent radicles appear to have approximately the same molecular refraction, although the numbers are different for hydrogen light. The displacement of hydrogen by chlorine in the benzene ring is attended by a great increase; also the displacement in the straight chain or in substituted benzenes, such as aniline, &c. The same holds in the case of the displacement by bromine, but as the numbers for chlorine or bromine differ greatly in the different series, it follows that the dispersion-free molecular refraction is not entirely additive, but is markedly dependent on the constitution. The entrance of two bromine atoms causes the same increase as that of one. Acetic, propionic, butyric, valeric, and isobutyric acids were also examined; in this case again the value obtained for the molecular refraction of acetic acid appears abnormally high. The dielectric constants for mixtures of different liquids was also observed in order to test whether the property was simply additive in mixtures; in many cases this appeared to be the case, but in others the found and calculated values do not agree.

L. M. J.

**Line Spectrum of Oxygen.** By M. EISIG (*Ann. Phys. Chem.*, [2], 51, 747—760).—The measurements by different observers of the

line spectrum of oxygen have been confined to single portions of the spectrum, have been made by different methods, and making use only of small dispersions. In order to obtain a complete set of comparative results, the author has therefore undertaken a careful examination of the complete oxygen spectrum, with the use of the concave grating employed by Kayser and Runge in their researches on the line spectra of the elements. The results are given in tabular form, and compared with those of Schuster, of Deslandres, of Trowbridge and Hutchins, and of Hartley and Adeney. No relationships between the reciprocals of the wave lengths, such as those obtained by Kayser and Runge in the case of other elements, are in any way evident, and a comparison with the solar spectrum also shows an absence of general coincidence between the lines of the oxygen spectrum and that of the sun.

H. C.

### Polarisation of a Thin Metal Partition in a Voltameter.

By J. DANIEL (*Phil. Mag.*, [5], 37, 185—201, and 288—300).—When a thin metal partition is introduced between the poles of a voltameter, gases are evolved at its surface, but if the thickness of the partition is below a certain limit, the current passes without evolution of gas and without evident polarisation. The author finds that the "critical thickness," that is, the least thickness of partition through which the current passes without polarisation, is 0.00009 mm. for gold, 0.00015 mm. for platinum, and 0.0005 mm. for aluminium, with a small current and a good conducting electrolyte. The "upper critical limit," that is, the smallest thickness for which the polarisation is the same as for very thick plates, is about 0.004 mm. under the above conditions. Between the critical limits, the polarisation increases with the thickness.

Special experiments indicated that in the case of copper sulphate solution, the passage of the current was not accompanied by the passage of copper ions through the gold-leaf partition, but rather that the copper sulphate itself diffused bodily through the membrane.

J. W.

**Dielectric Constants and Chemical Equilibrium.** By W. NERNST (*Zeit. physikal. Chem.*, 13, 531—536).—As the energy of an electrically charged system is lowered when placed in a medium of higher dielectric capacity, the author points out that there is hence an attractive force on electric points towards the medium with the higher capacity. From this he deduces, by considering the ions as electrically charged points, that the greater the dielectric constant,  $\kappa$ , of a medium, the greater will be the electric dissociation of a dissolved substance. Data for verification are few, but the known facts support this view, thus:—

	$\kappa$ .	Electric dissociation.
Gases .....	1.0	Not at ordinary temperatures.
Benzene .....	2.3	Very slight; traces.
Alcohol .....	25.0	Distinct.
Water.....	80.0	Very strong.

Experiments also on the dissociation of hydrogen chloride gave:

benzene, xylene, and hexane, very slight; ether, slightly stronger; then isobutylic alcohol, ethylic alcohol, and methylic alcohol, the order being the same as that of the dielectric capacity. Many organic acids contain molecular complexes, which decompose first into simple molecules and then into ions. The decomposition would also probably follow this law. This action is observable in the following order, according to the measurements of Eijkman and Beckmann; hydrocarbons ( $\kappa = 2.2-2.4$ ); carbon bisulphide ( $\kappa = 2.6$ ); chloroform ( $\kappa ?$ ); ether ( $\kappa = 4.4$ ); ethereal salts ( $\kappa = 6-9$ ); alcohols ( $\kappa = 16-33$ ); acids ( $\kappa ?$ ); and water ( $\kappa = 80$ ). A short indication is also given of a method for the simple and accurate determination of the constants.

L. M. J.

#### Minimum Electromotive Force necessary for Electrolysis.

By M. LE BLANC (*Compt. rend.*, 118, 702-707; and by BERTHELOT (*ibid.*, 707-709).—A question of priority (compare this vol., ii, 223).

C. H. B.

**Formation of Floating Metallic Films by Electrolysis.** By F. MYLIUS and O. FROMM (*Ann. Phys. Chem.*, [2], 51, 593-621).—During the electrolysis of a concentrated zinc sulphate solution, it was observed that the cathode wire became surrounded by a film of metallic zinc floating upon the surface of the solution, the film increasing gradually to a considerable size. A somewhat similar observation has been made by F. Kohlrausch in the case of the electrolysis of a solution of silver chloride in ammonia, and the authors have therefore been led to study the conditions under which the formation of such films take place. Experiments made with zinc sulphate and ammoniacal silver chloride show that the two principal necessary conditions are, an impure state of the surface of the solution, and the presence of oxygen in the atmosphere above the solution. If the surface is perfectly clean, formation of a film is not observed, whilst on the other hand, the addition of the smallest trace of any oily impurity, such as turpentine, which will float upon the surface, favours the film formation. If the air above the liquid is replaced by hydrogen, carbonic anhydride, or nitrogen, the film is not formed. Observations with both the zinc and silver films point to the presence of some trace of oxidised metal in the film, and if the surface of the solution is covered with an oil that has been completely freed from dissolved oxygen, the film is not formed. In other cases, the formation of a film below the surface of the liquid, as at the boundary between the solution and a heavy oil like chloroform, is possible. Films were also obtained from copper, cadmium, cobalt, iron, and antimony solutions. When the copper solution is treated with a solution of sulphur, in a mixture of benzene and carbon bisulphide, the surface film consists chiefly of cuprous sulphide, and a solution of iodine in benzene on the surface of silver sulphate gives rise to the formation of a silver iodide film.

H. C.

**Changes of Temperature caused by Contact of Liquids with Powdered Silica, &c.** By G. GORE (*Phil. Mag.*, [5], 37, 306-316).—Finely divided silica was brought into contact with



10 per cent. solutions of various substances, and the resulting rise of temperature noted; this rise varied with the nature of the substance dissolved, and increased with the fineness of the powder. Finely divided calcium carbonate, alumina, barium sulphate, and other substances were also tested, with similar results. J. W.

**Thermal Expansions of Solutions in Organic Solvents.** By G. TAMMANN and W. HIRSCHBERG (*Zeit. physikal. Chem.*, 13, 543—549).—It had been previously pointed out that the isobars of solutions at atmospheric pressure correspond with those of the solvent, if the latter are considered for a somewhat higher pressure (this vol., ii, 224); data were forthcoming in the case of water, but for other liquids hardly any were available. The authors' aim was therefore to verify experimentally the above conclusion. The expansions of various solutions in alcohol, ether, benzene, and carbon bisulphide were determined, the method used was the dilatometric, and the volumes were observed at four temperatures, 0°, 10°, 20°, and 30°; the results showing that the solutions were in all cases less expansible than the solvent. The expansions of alcohol and ether for pressures from 1 to 500 atmospheres were taken from the researches of Amagat (*Ann. Chem. Phys.* [6], 29, 518). Solutions of calcium chloride, sodium iodide, potassium acetate, mercuric chloride, potassium iodide, ammonium bromide, ammonium nitrate, ferric chloride, iodine, tartaric acid, salicylic acid, ethylic benzoate, borneol, and acetanilide in alcohol; and of benzoic acid, salicylic acid, naphthalene, and mercuric chloride in ether were examined, and for various concentrations, the pressure at which the expansion of the solvent agreed with that of the solution being determined.

The pressure  $\Delta$  divided by the concentration was approximately constant for different concentrations, the value sometimes increasing and sometimes decreasing with the temperature; this value,  $\Delta\pi/m$ , is noticeably less than the values for solutions in water, in which solvent also it is greater for electrolytes than for non-electrolytes.

L. M. J.

**Melting Point Determinations at a Red Heat.** By V. MEYER and W. RIDDLE (*Ber.*, 27, 766).—The authors have determined the melting points of certain salts with a larger (platinum) air thermometer than that previously used in determining the solidifying points (this vol., ii, 6). The new results agree roughly with the old ones, except in the case of sodium carbonate, the melting point of which is now found to be considerably lower than that of potassium carbonate, although still higher than those of sodium chloride or sulphate. C. F. B.

**Apparatus for Facilitating the Boiling of Liquids.** By V. GERNHARDT (*Ber.*, 27, 964—965).—An ordinary flask is fitted at the bottom with a short rod of red Jena fusible glass, in a similar manner to the platinum wire in Beckmann's boiling point apparatus; the advantages of the red glass are, its cheapness and freedom from risk of fracture on heating or cooling, whilst, owing to its high conductivity

and greater mass, the liquid is as readily heated as when platinum is employed. J. B. T.

**Separation of Three Liquids by Fractional Distillation.** By F. R. BARRELL, G. L. THOMAS, and S. YOUNG (*Phil. Mag.*, [5], 37, 8—31).—The authors calculate curves representing graphically the progress of the distillation of three liquids on the assumption that the proportion of the three substances in the vapour forming the instantaneous distillate is the same as that of the weights of the three substances in the residue in the still, each weight being multiplied by a suitable constant, which is roughly proportional to the vapour pressure of the corresponding liquid.

To test the validity of the results arrived at, a mixture of 200 c.c. of methylic acetate, 250 c.c. of ethylic acetate, and 200 c.c. of propylic acetate, was distilled from a flask provided with a still-head 1 metre long. After 26 preliminary fractionations, the liquid had been divided into two series of fractions, one series containing practically only ethylic and methylic acetates, the other series ethylic and propylic acetates. Six further fractionations separated the individual ethereal salts. The quantities of pure methylic, ethylic, and propylic acetates finally obtained were respectively equal to 48, 53, and 72 per cent. of the quantities originally taken. J. W.

**Law of corresponding Boiling Points.** By U. DÜHNING (*Zeit. physikal. Chem.*, 13, 492—499).—The paper is a claim for priority of enunciation of the law of corresponding boiling points, particularly with respect to E. Colot's and S. Young's claims. The author bases his claims on the expression of the law as  $t' = \gamma + qt$ , in a publication in 1878, and in *Ann. Phys. Chem.*, [2], 11, 164 (1880), in which expression,  $t'$  and  $t$  are the boiling points of two liquids at the same pressure, and  $\gamma$  and  $q$  are constants. L. M. J.

**Van der Waals's Corresponding States.** By S. YOUNG (*Phil. Mag.*, [5], 37, 1—8; compare *Abstr.*, 1893, ii, 63).—From his collected data for the corresponding pressures, volumes, and temperatures of 22 liquids in contact with their saturated vapours, the author shows that van der Waal's generalisations regarding "corresponding" states are approximately true within certain groups of substances, those examined by him falling into four chief series, namely,

I. Benzene, its halogen derivatives, carbon tetrachloride, stannic chloride, ether.

II. Methylic, ethylic, and propylic alcohols (methylic alcohol differing, however, considerably from the others).

III. Acetic acid.

IV. Ten ethereal salts.

The alcohols and acetic acid diverge most from the other substances, this being probably due to the molecular aggregation shown to exist in these liquids by Ramsay and Shields. J. W.

**Pressure of Saturated Vapours.** By K. D. KRAEVITCH (*Phil. Mag.*, [5], 37, 38—90).—The author finds that the following formula

may be used for calculating the vapour pressure of liquids at different temperatures with close approximation.

$$\text{Log } \frac{p}{p_0} = - \frac{c - c_1}{AD} \left( \log \frac{T}{T_0} - m \frac{T - T_0}{T} \right) + \frac{m\tau_0}{AD} \left( \frac{1}{T_0} - \frac{1}{T} \right).$$

Here  $p$  and  $p_0$  are the pressures at the absolute temperatures  $T$  and  $T_0$ ;  $c$  and  $c_1$  the specific heat of the vapour at constant volume and constant pressure;  $A$  the thermal equivalent of work;  $D$  the gas constant;  $\tau_0$  the latent heat of vaporisation, and  $m$  the modulus of the decadic logarithms.

The difference  $c - c_1$  is supposed to be constant throughout the ranges of temperature considered.

A comparison of the calculated values with experimental data is given for a large number of substances.

J. W.

#### Apparatus for Determining the Specific Gravity of Soft Fats.

By Z. ZIAWALKIEWICZ (*Monatsh.*, 15, 132—138).—The apparatus consists of a weighing bottle with two narrow necks. Of these, one comes from the base, and through it the just-molten fat enters from a reservoir placed above; the excess of fat passing out from the other neck into a small chamber. By this means the bottle is completely filled with fat, and air-bubbles are excluded. In order to control the temperature, the bottle and reservoirs are placed in a specially-arranged glass vessel which allows of the melting of the fat and the subsequent slow cooling to the point at which it is desired to determine the specific gravity. The paper is accompanied by a sketch of the apparatus, and gives numbers obtained for various fats.

G. T. M.

#### Determination of Small Dissociation Tensions of Hydrated Salts.

By C. E. LINEBARGER (*Zeit. physikal. Chem.*, 13, 500—508).—The author points out that if a substance is dissociated by a liquid into soluble and insoluble components, the partial pressure of the former, when equilibrium occurs, must be equal to the dissociation tension of the substance, and if, further, for this constituent the partial pressure is known at different concentrations and temperatures, then the dissociation tension may be determined by finding the quantity of the soluble constituent dissolved. A number of hydrated salts in ether are thus examined. A table is first given connecting the quantity of water dissolved with the lowering of the boiling point of the ether. By means of Nernst's formula

$$p = 39 \frac{mx}{1.315 \times 0.58},$$

(where  $p$  = partial pressure,  $m$  = quantity of water, and  $x$  proportion of double mols. dissociated) a table is next set out giving the partial pressure of water for every  $0.01^\circ$  lowering of the boiling point of ether. Determinations are then recorded of this lowering by the addition of several hydrated salts, namely, cupric sulphate, strontium chloride, magnesium sulphate, zinc sulphate, barium chloride, man-

ganese sulphate, and ferrous sulphate, and the partial pressure of the dissolved water then calculated. This is equal to the dissociation tension of the salt.

In the first four cases, the results are compared with those of Frowein (Abstr., 1888, 337), and are seen to be quite concordant. In the cases, however, of barium chloride and ferrous sulphate, no trustworthy results could be obtained.

L. M. J.

### Dissociation of Potassium Triiodide in Aqueous Solution.

By A. A. JAKOVKIN (*Zeit. physikal. Chem.*, 13, 539—542).—The dissociation can be studied by allowing a solution of iodine in potassium iodide solution to remain in contact with carbon bisulphide until equilibrium is reached; any iodine formed by the dissociation (non-electrolytic) must divide itself between the two solvents in a constant ratio independent of concentration. As the partition ratio for carbon bisulphide and water is 410 : 1, the quantity of free iodine in the solution can be estimated by analysing the carbon bisulphide.

The constant of dissociation according to the equilibrium equation  $KI_3 \rightleftharpoons KI + I_2$  is calculated by the formula  $k = \frac{(a - 1 + x)x}{v(1 - x)}$ , where  $a$  is the ratio of mols. of KI to mols.  $I_2$ , and  $x$  is the ratio of free to total iodine,  $v$  being the volume per gram molecule of iodine. From 32 experiments with varying concentrations of iodine and of potassium iodide, a mean value  $k = 1683 \times 10^{-6}$  was found, the individual numbers varying from 1577 to 1808, with a mean difference of about 2 per cent. If the value of  $k$  be calculated for other equilibrium equations, e.g.,  $KI_3 \rightleftharpoons KI + 2I_2$ , the value of  $k$  varies within very wide limits, 10180 to 461,  $\times 10^{-4}$ . From this the author concludes that there are certainly  $KI_3$  molecules in this solution, and that the law of Henry extends to undoubtedly chemical and partly dissociated solutions.

L. M. J.

**The Hydrolysis of Weak Acids and Bases.** By S. ARRHENIUS (*Zeit. physikal. Chem.*, 13, 407—411).—The author examines some of the results of Lellmann and Schliemann (Abstr., 1893, ii, 407) which the latter had considered were not in accordance with the dissociation theory as at present understood. The author, therefore, calculates from the basis of this theory the ratios of the extinction coefficients of solutions of helianthin in acetic, propionic, hydroxyisobutyric, chloracetic, and trichloracetic acids, and compares them with the observed numbers of Lellmann. The results are shown in

Acetic Propionic		Hydroxyisobutyric Acetic		Monochloracetic Hydroxyisobutyric		Trichloracetic Monochloracetic	
Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
1.08	1.04	1.12	1.16	1.12	1.08	1.08	1.05
1.20	1.06	1.25	1.28	1.23	1.16	1.11	1.07
1.37	1.09	1.40	1.44	1.32	1.28	1.14	1.09

the table (p. 271), the horizontal line corresponding with three different concentrations in ratio 1 : 4 : 16, the upper line being the strongest. L. M. J.

**General Law of Solubility of Normal Substances.** By H. LE CHATELIER (*Compt. rend.*, 118, 638—641).—If the latent heat of solution of a substance is considered as equal to its latent heat of fusion, the author shows that the following relationship may be developed from established laws respecting the behaviour of solutions:—

$$0.002 \log s - \frac{L}{t} + \frac{L}{t_0} = 0,$$

where  $s$  is the concentration of the dissolved substance expressed as the number of molecules of this substance in 1 mol. of the solution,  $L$  is the latent heat of fusion,  $t_0$  the melting point of the dissolved substance, and  $t$  the solidifying point of the solution. As the equation contains no term relating to the solvent, the conclusion is evident that the curve of solubility of a given substance in any solvent will always be of the same form. H. C.

**Mutual Solubility of Salts.** By H. LE CHATELIER (*Compt. rend.*, 118, 709—713).—In the determination of the solubility of salts one in another, or, what comes to the same thing, of the fusing points of saline mixtures, three general cases may be distinguished.

1. The salts solidify to form isomorphous mixtures of variable composition.

2. Each salt solidifies separately from the mixture.

3. The two salts combine and solidify as a compound of definite composition.

Cases of the first kind have already been considered by the author, and also by Küster (*Abstr.*, 1892, 396), and in the present paper instances of the second kind are recorded. The solubilities of sodium chloride and of lithium sulphate in various salts were measured by determining the fusing points of the saline mixtures. The following table gives the results.

		Melting points.				
Substance.	Solvent. $s =$	1.	0.9.	0.8.	0.7.	0.6.
NaCl .....	Na <sub>2</sub> CO <sub>3</sub> .....	778	755	—	718	692
„ .....	Pb(NO <sub>3</sub> ) <sub>2</sub> .....	—	762	742	710	—
„ .....	BaCl <sub>2</sub> .....	—	758	740	—	690
„ .....	Calculated. ....	—	758	738	717	694
Li <sub>2</sub> SO <sub>4</sub> .....	CaSO <sub>4</sub> .....	830	750	675	—	—
„ .....	Li <sub>2</sub> CO <sub>3</sub> .....	—	745	667	580	—
„ .....	Na <sub>2</sub> SO <sub>4</sub> .....	—	750	680	620	—
„ .....	Calculated. ....	—	741	661	580	—

*s* in this table is the concentration of the dissolved substance, and the calculated values were obtained, making use of the formula developed by the author (see preceding abstract). The latent heats of fusion per gram molecule of the dissolved salts deduced from these results are 12.6 cal. for NaCl and 5.68 cal. for  $\text{Li}_2\text{SO}_4$ . That the solubility is independent of the nature of the solvent, as predicted (*loc. cit.*), is in so far confirmed by these determinations. H. C.

**Solubility of Mercuric and Sodium Chlorides in Ethylic Acetate.** By C. E. LINEBARGER (*Amer. Chem. J.*, 16, 214—216).—Continuing his work on this subject (*Abstr.*, 1893. ii, 450), the author gives a table and a curve of the solubility of mercuric chloride in ethylic acetate in the presence of varying proportions of sodium chloride. Determining the separate solubilities of the two salts, 100 mols of ethylic acetate at 40° dissolved 16 mols. of mercuric chloride, but only 0.037 mol. of sodium chloride; when, however, a mixture of the chlorides was treated, a solution was obtained which contained 40 mols. mercuric chloride, and 20 mols. of sodium chloride, to 100 mols. of ethylic acetate. The influence of the sodium chloride is first to somewhat reduce the solubility of the mercuric chloride, such influence being greatest when two molecules of sodium chloride have gone into solution in 100 mols. of the solvent (the solubility of the mercuric chloride being then 12 mols. in 100). The solubility of both salts then increases, at first slowly, then more rapidly.

L. T. T.

**Saturated Solutions.** By R. LÖWENHERZ (*Zeit. physikal. Chem.*, 13, 459—491).—The paper contains researches on the saturated solutions containing potassium and magnesium chlorides and sulphates in all their possible combinations. The results are expressed graphically by taking the four edges which meet at the corner of a regular octahedron as the axis, and marking along them, in order, the solubility of potassic sulphate, potassic chloride, magnesium chloride, and magnesium sulphate. Upon each of the faces between two of these edges, for instance, the  $\text{K}_2\text{SO}_4 : \text{K}_2\text{Cl}_2$  are then lines representing the effects of the addition of one of these salts on the solubility of the other, so that the point where the two lines meet represents the composition of the solution saturated by both salts. Lines similarly drawn from these points into the space of the solid angle represent the effect of the other salts on the saturation composition of these solutions, so that the space is ultimately closed by a surface divided into fields which give the composition of solutions saturated with the salts  $\text{KCl}$ ;  $\text{K}_2\text{SO}_4$ ;  $\text{MgCl}_2$ ;  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ ;  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ; carnallite; and schönite. The lines separating the fields correspond with solutions saturated by two of these salts, and the points where the lines meet represent solutions saturated by three substances which are present as solids in contact with the solutions. Some of the data were already known, but most had to be experimentally determined, as the solubility of  $\text{MgCl}_2$ ;  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ;  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ ;  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ ; carnallite and  $\text{KCl}$ ; and the composition of solutions saturated with three salts. From the figure thus obtained, it is possible to calculate

what substance will first crystallise out from a solution of any given composition, and what substance next, &c. A number of experiments performed gave in all cases results which agreed with those thus deduced.

L. M. J.

**Molecular Weight in Solid Solutions.** By F. W. KÜSTER (*Zeit. physikal. Chem.*, 13, 445—458).—In order to determine with what molecular weight ether is dissolved in caoutchouc, the author studies the lowering of the freezing point of water, owing to ether in the presence of caoutchouc. The substances employed were carefully purified, and the lowering of the freezing point by ether alone was first determined. A figure of the apparatus employed is given, being a Beckmann thermometer in a well-jacketed flask. The caoutchouc was found to exercise no effect on the freezing point of the water, and in the case of water, ether and caoutchouc equilibrium was found to occur in about  $1\frac{1}{2}$  hours. A number of experiments are then recorded, made, at the freezing point of the solution, with 50 c.c. of water, 5 c.c. of ether, and varying quantities of caoutchouc. From the lowering of the freezing point, the quantity of ether dissolved in the water is calculated, and hence that dissolved in the caoutchouc. The percentage volume concentration in the two solvents is thus known. If  $O_k$  be this concentration in the caoutchouc and  $C_w$  in the water, the results gave  $C_k/C_w = 1.21; 1.55; 1.69; 1.81$ , and  $\sqrt{C_k}/C_w = 0.435; 0.466; 0.473; 0.469$ ; the higher numbers corresponding with the smaller quantity of caoutchouc. It thus appears that the caoutchouc molecules contain abnormal molecules of ether, and from the approximate constancy of  $\sqrt{C_k}/C_w$  probably double molecules. The next series of experiments were at a temperature of  $18-16^\circ$ , and were made with 50 c.c. water, 10 grams caoutchouc, and quantities of ether varying from 1 to 14 c.c. The ratio of  $C_k/C_w$  varied from 3.10 to 5.36, and that of  $\sqrt{C_k}/C_w$  from 1.58 to 0.76. The increase with concentration is, as would be expected, slower than at low temperatures, while the decrease of the numbers  $\sqrt{C_k}/C_w$  indicates a smaller number of double molecules in the more dilute solutions, and also that they become very numerous in higher concentrations. The ratio  $C_k/C_w$  is calculated as 2.8 for infinite dilution, where all molecules are simple. The ratio of the number of the *simple* molecules in the two solvents, however, must be independent of the concentration. Hence the value  $2.8 C_w = C_k$  gives the concentration of simple molecules in the caoutchouc, and the difference  $C_k - 2.8 C_w = C''_k$ , the concentration of the complex molecules. If they are really double molecules, the equation  $(C'_k)^2 = KC''_k$  should obtain. The values of the ratio  $C'_k/\sqrt{C''_k}$  are deduced and are approximately constant, varying, in 11 experiments, from 5.3 to 5.8. A series of experiments performed at  $0^\circ$  are similarly treated, and for low concentration the value  $\sqrt{C_k}/C''_k$  only varies between 3.0 and 3.3. For very high concentrations, however, it decreases considerably.

L. M. J.

**Velocity of Hydrolysis of some Ethereal Salts.** By A. DE HEMPTINNE (*Zeit. physikal. Chem.*, 13, 561—569).—The author deter-

mines the velocity of hydrolysis of 11 of the lower ethereal salts, the reaction being induced by hydrochloric acid in a N/20 solution of the salt, at a temperature of 25°. The values for  $K$ , calculated by the formula  $K = \frac{1}{t} \log \frac{A}{A-x}$  are given in the table.

	Acetate.	Ratio.	Propionate.	Ratio.	Butyrate.
Methylic ..	0.001432	1.074	0.001538	1.797	0.0008560
Ratio ..	0.9670		0.9736		
Ethylic. . .	0.001481	1.066	0.001580	1.744	0.0009061
Ratio ..	1.016		1.004		
Propylic ..	0.001458	1.078	0.001573	1.781	0.000883
Ethylic isobutyrate, 0.000889; ethylic valerate, 0.000312.					

The values calculated for the same units as Reicher's numbers may be obtained from the above by multiplying by 4.624. It is seen from the equality of the ratios for the same series, that if the velocities for one series are known, those for another can be calculated from that of one of its members. The nature of both acid and alcohol is seen to affect the rate. Comparison made with Reicher's numbers for hydrolysis by sodium hydroxide show that the action of the hydroxyl ions is greater than that of the hydrogen ions. The author also describes some experiments made to discover whether the acid exerted any catalytic action in the gaseous state. A gaseous mixture of ethylic acetate and hydrogen chloride was kept for two hours at a temperature of 210°, when it was found that 15 per cent. of the salt was hydrolysed. The author does not consider, however, this can yet be stated to be due to free ions.

L. M. J.

**Endothermic Reactions effected by Mechanical Force.** By W. SPRING (*Zeit. anorg. Chem.*, 6, 176).—Carey Lea ignores the author's work when he claims (this vol., ii, 85) that, before himself, no one had accomplished the conversion of mechanical into chemical energy. Eleven years ago the author expressly wrote (*Bull. Acad. Belg.*, [3]. 5):—"The facts to which I have just called attention prove conclusively that it is possible to cause substances to react chemically by means of mechanical energy alone."

C. F. B.

**Phases and Conditions of Chemical Change.** By V. H. VELEY (*Phil. Mag.*, [5], 37, 165—184).—The author distinguishes four stages through which chemical actions pass, namely, (1) a period of commencement, (2) of inertness, or reluctance followed by acceleration, (3) of constancy, (4) of diminution of velocity; and gives examples illustrating this division. He then proceeds to discuss the nature of chemical change, and the cause of its commencement, criticising adversely Armstrong's reversed electrolysis theory, Arrhenius' theory of electrolytic dissociation, and the notion of nascent action.

J. W.

**Expenditure of Energy Equivalent to the Chemical Action of Light.** By G. LEMOINE (*Compt. rend.*, 118, 525—528).—In studying the action of oxalic acid on ferric salts (*Abstr.*, 1893, ii, 405), no account was taken of the possible influence of light on the



course of the reaction. It has now been ascertained, experimentally, that this influence is practically inappreciable, and that light probably plays no part beyond that of aiding in inducing the reaction in question. H. C.

**Employment of Electricity to follow the Phases of certain Chemical Reactions.** By J. GARNIER (*Compt. rend.*, 118, 588—589).—A mixture of nickel oxide and wood charcoal was placed in an earthenware tube, closed by two plugs of soft steel, by which the mixture was compressed. The two steel plugs were placed in an electric circuit, and the earthen tube, supported horizontally, was heated in a small reverberatory furnace. The resistance of the powder in the tube was at first extremely high, but gradually became less and less, until it became almost nil. It then increased again, finally becoming very high. The decrease of resistance corresponds with the gradual reduction of the oxide, the reduction being complete at the moment when the resistance was almost nil; as the nickel became carburetted, however, the resistance increased.

In a similar experiment, with a mixture of copper, iron, and nickel oxides and wood charcoal, the successive phases of reduction were indicated by the variations in the resistance. In the same manner, the process of refining might be followed, and the method has the advantage that the readings of the ammeters and voltmeters can be made at a point removed from the position of the furnace, &c.

C. H. B.

**Accurate Determination of Atomic Weights, using Silver as a Secondary Standard.** By G. HINRICHS (*Compt. rend.*, 118, 528—531).—Comparing the results obtained by Dumas, Stas, and Cooke for the atomic weight of sulphur, referred to that of silver taken as 108, the author maintains that the atomic weight found is a function of the amount of silver taken. The following table of comparison is given.

	No. of experiments.	Wt. of Ag in grams.	At. wt. found.
Cooke .....	2	1.0	32.004
Dumas.....	2	10.0	31.998
Dumas.....	3	30.7	32.028
Stas.....	7	164.8	32.084

If  $\eta$  is the atomic weight found for sulphur, and  $w$  the weight of silver used,  $\eta = 0.001 w - 0.000003 w^2$ . Similar results are obtained for chlorine, bromine, and the other elements whose atomic weights were determined by Dumas and Stas.

The author applies his method of limits to these results, and for  $w = 0$  finds the atomic weights Cl = 35.5, Br = 80, I = 127, and S = 32 exactly when Ag is taken as 108. H. C.

**Crystalline Structure.** By W. NERNST (*Zeit. physikal. Chem.*, 13, 537—538).—A reply to an observation of Retgers (*Zeit. physikal.*

*Chem.*, 12, 621), in which the author claims to have been misquoted by the former, and contests, although without discussion, the accuracy of his statement, that several amorphous bodies behave, in certain of their physical properties, as if composed of crystalline fragments too small for direct perception. L. M. J.

## Inorganic Chemistry.

**Occurrence of Hydrogen Peroxide in the Air.** By L. ILOSVAY DE N. ILOSYA (*Ber.*, 27, 920—925).—In reply to Schöne (this vol., ii, 88), the author maintains that, owing to the presence of nitrogen peroxide as a constant constituent of the atmosphere, the evidence hitherto brought forward to establish the presence of ozone and hydrogen peroxide in the air or in rain water, is insufficient. The oxidising effects which have been observed are all due to this agent, and when this is removed, no evidence of the presence of any other oxidising agent more powerful than free oxygen can be found.

A. H.

**Hydrogen Peroxide in the Atmosphere.** By E. SCHÖNE (*Zeit. anal. Chem.*, 33, 137—184).—This discussion of the results of Ilosvay de Ilosva covers precisely the same ground as that communicated to the *Ber.* (this vol., ii, 88), but with more minuteness of detail.

M. J. S.

**Ratio of the Atomic Weights of Oxygen and Hydrogen.** By J. THOMSEN (*Zeit. physikal. Chem.*, 13, 398—406).—The method employed was an indirect one, in which the ratio of the molecular weights of hydrogen chloride and ammonia was determined. If the ratio  $\text{NH}_3/\text{HCl} = \gamma$ , then it follows that the atomic weight of hydrogen, in terms of Cl and N, is given by the equation 
$$\text{H} = \frac{\gamma\text{Cl} - \text{N}}{3 - \gamma}$$

Pure dry hydrogen chloride was first passed into pure distilled water, and the increase in weight found; it was then neutralised as nearly as possible by pure ammonia, and the increase of weight again observed. The liquid was finally exactly neutralised by a standard solution, which contained 0.01703 gram of hydrogen chloride per gram. The mean of 17 experiments, with quantities of water varying from 100 to 200 grams, and from 4 to 19.4 grams of hydrogen chloride gave the ratio  $\text{HCl}/\text{NH}_3 = 2.14087$ , with a probable error of  $\pm 0.00009$ , or, when corrected for vacuum weighings,  $\text{HCl}/\text{NH}_3 = 2.13934 \pm 0.00009$  and  $\gamma = 0.467433 \pm 0.000019$ .

The atomic weights of hydrogen are then calculated from the values of Stas, Ostwald, and Von der Plaats, for chlorine and nitrogen (referred to O = 16).

	Stas.	Ostwald.	Von der Plaats.
Cl .....	35.457	35.4529	35.4565
N .....	14.044	14.0410	14.0519
H .....	0.9989	0.99946	0.9959

The probable error is given in the ratios  $dH = 14.4 d\gamma$ ,  $\alpha H = 0.185 dCl$ , and  $dH = 0.393 dN$ .

If Stas' value for chlorine, and Ostwald's value for nitrogen, be taken, the ratio of the weights of oxygen and hydrogen becomes exactly 16 : 1, which is, therefore, as near the true ratio as the accuracy of present data allows. L. M. J.

**Phenomena of Oxidation and Chemical Properties of Gases.** By F. C. PHILLIPS (*Amer. Chem. J.*, 16, 163—187, 235—254).—See this vol., ii, 293, 294.

**Stability and Preparation of Free Hydroxylamine.** By C. A. LOBBY DE BRUYN (*Ber.*, 27, 967—970).—A number of specimens of hydroxylamine, prepared by the author in September, 1891, have been analysed; one, which had been kept in a cellar, solidified at  $28.5^{\circ}$ , contained 93 per cent. of hydroxylamine and a trace of ammonia, but no nitrous acid; pure hydroxylamine solidifies at  $33^{\circ}$ . Hydroxylamine is tolerably stable at temperatures up to  $15^{\circ}$ , the decomposition proceeds gradually, ammonia, nitrous acid, and hyponitrous acid are first formed, and these, together with the unaltered hydroxylamine, interact with production of nitrogen and nitrous oxide. Hydroxylamine hyponitrite is probably too unstable to exist, as the nitrite decomposes above  $20^{\circ}$  in methylic alcoholic solution; only one of the above specimens of hydroxylamine contained a trace of hyponitrous acid. The alkalinity of the glass vessels in which the hydroxylamine is preserved greatly facilitates its decomposition.

The paper contains a number of details regarding the preparation of hydroxylamine, and a discussion of Bruhl's communication (this vol., i, 9) on the subject. J. B. T.

**Composition and Heat of Formation of the Hydrate of Nitrous Oxide.** By VILLARD (*Compt. rend.*, 118, 646—649).—The hydrate of nitrous oxide (Abstr., 1888, 1020) was formed from water and liquid nitrous oxide in a glass tube, and the latter was cooled below  $0^{\circ}$  and the excess of gas allowed to escape. The composition of the hydrate was determined by measuring the volume of gas given off on heating, and five experiments gave results varying between  $N_2O, 5.9H_2O$  and  $N_2O, 6.44H_2O$ , and hence, in all probability, the true composition is  $N_2O, 6H_2O$ . Experiments made by measuring the volume of the liquid nitrous oxide before combination with a known quantity of water, and the volume of the oxide in excess, gave  $N_2O, 6.6H_2O$  and  $N_2O, 6.3H_2O$ .

Direct measurements in the calorimeter gave the following results:—

Formation of hydrate from the dissolved gas (water,	
1 gram) .....	= 77.8 cal.
Dissolution of the corresponding gas .....	= 57.5 „
Formation of the hydrate from the gas and water ..	= 139.0 „

The crystals of the hydrate have no action on polarised light, and show distinct octahedral terminations; they, therefore, seem to belong to the regular system. C. H. B.

**Carbon Boride.** By H. MOISSAN (*Compt. rend.*, 118, 556—560).—Carbon boride is formed when the electric arc is allowed to pass between two carbons agglomerated by means of a solution of boric acid and aluminium silicate, or when boron is placed in the electric arc, but much larger quantities can be obtained by heating a mixture of 66 parts of amorphous boron and 12 parts of carbon from sugar in the electric furnace for six or seven minutes with a current of 250—300 amperes and 70 volts. It forms a black, graphitoidal mass with a brilliant fracture, and after prolonged treatment with fuming nitric acid, followed by potassium chlorate and nitric acid, a crystalline powder remains.

Another method is to add an excess of boron and carbon to some iron and heat the mixture in the electric furnace. A regulus with a very brilliant fracture is obtained, and after treatment with aqua regia a residue is left, which consists almost entirely of carbon boride in badly defined crystals, which can be further purified by means of nitric acid and potassium chlorate.

Owing to the ease with which iron dissolves boron, better results are obtained by heating the mixture of boron and carbon with silver or copper; with the former the product is pure, but is confusedly crystalline; with the latter the crystals are well defined. 15 grams of the mixture of carbon and boron is heated with 150 grams of copper in the electrical furnace for six or seven minutes with a current of 350 amperes and 70 volts. The product is treated with nitric acid, and afterwards with the acid and potassium chlorate.

Boron carbide, prepared by any of these methods, has the composition  $\text{CB}_2$ , and forms brilliant, black crystals of sp. gr. 2.51. It is attacked by chlorine below  $1000^\circ$  without incandescence, but it is not affected by bromine or iodine, or by sulphur, at the softening point of glass, or by phosphorus or nitrogen at  $1200^\circ$ . It is not attacked by boiling acids, or when heated in sealed tubes at  $150^\circ$  with chromic acid, fuming nitric acid, or a concentrated solution of iodic acid. When heated in oxygen at  $500^\circ$ , no carbonic anhydride is formed, but at  $1000^\circ$  the carbide burns slowly and with greater difficulty than the diamond, yielding carbonic anhydride, and a black residue surrounded by fused boric anhydride. At a dull red heat, carbon boride is attacked by potassium hydroxide, or by a fused mixture of potassium and sodium carbonates.

Carbon boride is very friable, but is also very hard, and although slightly softer than the diamond, it can be used to polish the latter, and produces very distinct facettes.

C. H. B.

**Potassium Double Salts of Hypophosphoric acid.** By C. BANSI (*Zeit. anorg. Chem.*, 6, 128—142 and 143—160).—The sodium hydrogen salt of the acid,  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_6$ , was first prepared by immersing sticks of phosphorus, all but about 1 cm. of each, in a 25 per cent. solution of sodium acetate; it separated in crystalline crusts. It was converted, by means of barium chloride, into the barium hydrogen salt, and this, by means of potassium sulphate, into the potassium hydrogen salt. By adding, to a strong solution of the latter, solutions of salts of the heavy metals, amorphous precipitates were first

obtained, consisting of the normal hypophosphates of the heavy metals, but these gradually took on a crystalline form, becoming converted into the acid potassium double salts. The latter were dried on a porous plate and analysed at once; they were not washed, as water decomposes them. By neutralising a solution of potassium hydrogen hypophosphate with caustic potash, a solution of normal potassium hypophosphate was obtained; on adding solutions of heavy metals to this, amorphous precipitates of the normal hypophosphates were at first formed, but gradually became converted into the normal potassium double salts. The acid double salts, when heated in the air, seem to form first pyrophosphates and then metaphosphates, but hydrogen is evolved, and some hydrogen phosphide.

*Acid Double Salts*—Those of *nickel* (green), *cobalt* (pink), *zinc*, and *copper* (blue), with potassium, form crystals of the rhombic system, and are isomorphous, having the composition  $M''H_2P_2O_6 \cdot 3K_2H_2P_2O_6 + 15H_2O$ . The *cadmium*,  $CdH_2P_2O_6 \cdot K_2H_2P_2O_6 + 2\frac{1}{2}H_2O$ , and the *manganese*,  $MnH_2P_2O_6 \cdot K_2H_2P_2O_6 + 3H_2O$ , potassium double salts are colourless.

*Normal Double Salts*.—The *nickel*,  $NiK_2P_2O_6 + 6H_2O$ , and *cobalt*,  $CoK_2P_2O_6 + 5H_2O$ , potassium double salts were prepared, they are respectively green and pink. The *potassium sodium* double salt,  $K_2Na_2P_2O_6 + 9H_2O$ , can be obtained by neutralising the potassium hydrogen salt with sodium carbonate; the same substance is obtained when the sodium hydrogen salt is neutralised with potassium carbonate. It forms colourless crystals belonging to the rhombic system,  $a : b : c = 1.0728 : 1 : 1.0845$ . C. F. B.

**Action of Nitrogen, Nitrous Oxide, and Nitric Oxide on Alkali Amides.** By A. JOANNIS (*Compt. rend.*, 118, 713—716).—Nitrogen has no action on solutions of the alkali metals in liquid ammonia.

When nitrous oxide acts on the solution, the principal reaction is  $N_2O + N_2H_5K = KNH_2 + NH_3 + KOH + N_2$ . If, however, the passage of the gas is continued after the liquid has been decolorised, the reaction,  $2NH_2K + N_2O = N_3K + KOH + NH_3$ , takes place. By reason of this reaction, a small quantity of the nitride  $N_3K$  is formed even before the solution has been decolorised.

Sodammonium behaves in a similar manner, and it is noteworthy that the formation of the nitride  $N_3Na$  proves that the product of the first action is  $NaNH_2 + NaOH$ , and is not the compound  $NH_3Na_2O$ , which is obtained by the action of oxygen on sodammonium.

Nitric oxide is absorbed by a solution of sodammonium or potassium-ammonium in liquefied ammonia, the blue colour disappearing and a pinkish, gelatinous product being formed, which, when the ammonia has evaporated, remains as an amorphous powder. The products thus obtained are sodium hyponitrite and potassium hyponitrite respectively. C. H. B.

*Note by Abstractor.*—The formation of the nitride  $N_3Na$  from solid sodamide and gaseous nitrous oxide has already been observed by W. Wislicenus (*Abstr.*, 1892, 1151). C. H. B.

**Atomic Weight of Barium.** By T. W. RICHARDS (*Zeit. anorg. Chem.*, 6, 89—127).—Two series of determinations were made with great care. In the first, the ratio  $2\text{AgCl}:\text{BaCl}_2$  was determined, the barium chloride employed having been (1) ignited in air and corrected for oxide and carbonate formed, (2) ignited in hydrogen chloride, or (3) crystallised and merely dried. The barium chloride was precipitated with excess of a solution of silver in nitric acid, and the precipitate collected and weighed. In the second series, the ratio  $2\text{Ag}:\text{BaCl}_2$  was determined, the barium chloride being precipitated by a slight excess of the solution of silver, and the excess of the latter determined in one of four different ways.

Assuming the atomic weights  $\text{Cl} = 35.456$ ,  $\text{H} = 1.0075$ ,  $\text{Ag} = 107.930$ , the two series give respectively the values 137.439 (10 experiments; maximum deviation  $+0.042$  and  $-0.022$ ) and 137.440 (14 experiments; maximum deviation  $+0.042$  and  $-0.057$ ). Including the results obtained with barium bromide (*Abstr.*, 1893, ii, 463), the mean result is 137.434; omitting certain determinations made by methods which are deemed less trustworthy, we have 137.441. It is sufficient to take as the final result  $\text{Ba} = 137.44$ . C. F. B.

**Specific Gravity of Fused Magnesium Oxide.** By H. MOISSAN (*Compt. rend.*, 118, 506—507).—The sp. gr. of magnesium oxide increases with the temperature at which it has been heated. Ditte obtained the following values: at  $350^\circ$ , 3.1932; at a dull red heat, 3.2482, and at a bright red heat, 3.5699. The author has obtained the following values at higher temperatures. After heating in a wind furnace for ten hours, 3.577; after heating in the electric furnace for two hours, 3.589; after fusing in the electric furnace, 3.654. It would seem that the polymerisation of the magnesium oxide continues up to its melting point. C. H. B.

**Crystallised Normal Magnesium Carbonate.** By K. KIPPENBERGER (*Zeit. anorg. Chem.*, 6, 177—194).—If freshly precipitated magnesium carbonate, made by mixing equivalent amounts of magnesium sulphate and sodium carbonate, is shaken with a solution of potassium hydrogen carbonate at the ordinary temperature, much of the magnesium carbonate dissolves, and crystallises out of the filtered solution after a time; the separation is ended in 24 hours. The same occurs if sodium hydrogen carbonate is used; it dissolves relatively more of the magnesium carbonate, but the crystals obtained are smaller. Solutions containing respectively 67.5 grams of potassium and 12.96 grams of sodium hydrogen carbonate per litre dissolved, respectively, 18.73 and 9.95 grams of magnesium carbonate. The crystals have the composition  $4\text{MgCO}_3 + 15\text{H}_2\text{O}$ ; after four weeks in dry air, or 15 hours in a vacuum desiccator over sulphuric acid, they have the composition  $2\text{MgCO}_3 + 5\frac{1}{2}$  (or 6)  $\text{H}_2\text{O}$ ; after heating at  $170^\circ$  the composition  $\text{MgCO}_3 + \frac{1}{2}$  (or  $\frac{1}{3}$ )  $\text{H}_2\text{O}$ . The reaction is, according to the author, that a double sesquicarbonate of magnesium and the alkali metal is formed, and that this afterwards decomposes, magnesium carbonate being precipitated, and carbonic anhydride liberated, which latter regenerates the alkali bicarbonate with the alkali sesquicarbonate now present.

Alkali bicarbonates do not dissolve calcium carbonate or ferric hydroxide, and upon this fact the author bases a technical process for the preparation of pure magnesium carbonate from dolomite, magnesite, and bitterspar, and from kainite or carnallite liquors. The mineral is powdered, dissolved in commercial hydrochloric acid, and the iron oxidised by warming gently with a little nitric acid. The solution is then precipitated with sodium carbonate in slight excess, the filtered precipitate shaken with a sufficiently strong solution of alkali bicarbonate, and the solution filtered after the lapse of 20 minutes, and set aside to crystallise. The mother-liquor can be used again and again for the extraction. C. F. B.

**Thallium Hypophosphates.** By A. JOLY (*Compt. rend.*, 118, 649—650)—*Dithallous hypophosphate*,  $\text{Th}_2\text{H}_2\text{P}_2\text{O}_6$ , is obtained by exactly neutralising a solution of hypophosphoric acid with thallium carbonate in presence of methyl-orange, or by the action of a boiling aqueous solution of thallium sulphate on monobarium hypophosphate. It forms anhydrous, colourless, transparent, and highly refractive monoclinic prisms. When heated somewhat below  $200^\circ$ , it melts suddenly and is converted into phosphate, and if heated above  $200^\circ$ , hydrogen phosphide is given off.

*Tetrathallous hypophosphate*,  $\text{Th}_4\text{P}_2\text{O}_6$ , is almost insoluble in cold water and is prepared by mixing boiling aqueous solutions of thallium sulphate and disodium hypophosphate in the calculated proportions. It separates in anhydrous, small, very slender, colourless, silky needles, and may be washed with cold water, and recrystallised from boiling water. When heated at about  $250^\circ$ , it suddenly liquefies with development of heat, but without loss of weight, and becomes black, being converted into a mixture of thallium metaphosphate and reduced thallium,  $\text{Th}_4\text{P}_2\text{O}_6 = 2\text{TiPO}_3 + \text{Th}$ . If the salt is quite dry no hydrogen phosphide is given off.

When exposed to direct sunlight, tetrathallous hypophosphate becomes indigo-blue at the surface, as if the same change were produced as under the influence of heat. C. H. B.

**Molecular Weight of Ferric Chloride.** By P. T. MULLER (*Compt. rend.*, 118, 644—646).—The author has determined, by Raoult's ebullioscopic method, the molecular weight of anhydrous ferric chloride in solution in alcohol and ether. The results are given in the following table,  $p$  being the weight of ferric chloride in 100 grams of the solvent,  $E$  the rise in the boiling point, and  $M$  the molecular weight given by the expression  $M = Kp/E$ , in which  $K$  is a constant with the value 11.5 in the case of alcohol and 21.1 in the case of ether.

<i>Alcoholic Solution.</i>			<i>Ethereal Solution.</i>		
$p$ .	$E$ .	$M$ .	$p$ .	$E$ .	$M$ .
2.860	0.21°	156.62	11.467	1.21°	200.0
4.416	0.31	163.8	6.985	0.86	171.3
6.556	0.47	160.41	2.888	0.42	145.0
10.132	0.72	161.83	2.006	0.28	151.1

It is clear that when dissolved in boiling alcohol or ether, the molecular weight of ferric chloride is represented by the formula  $\text{FeCl}_3$ . In the ethereal solution the molecular weight is lower the more dilute the solution. C. H. B.

**Alloys of Nickel and Iron.** By F. OSMOND (*Compt. rend.*, 118, 532—534).—The alloys investigated had the following composition:—

	A.	C.	E.	G.	J.	K.	L.	M.	N.
Carbon....	0.19	0.13	0.19	0.17	0.23	0.19	0.16	0.14	0.16
Silicon....	0.31	0.23	0.20	0.28	0.24	0.27	0.30	0.38	0.31
Manganese.	0.79	0.72	0.65	0.68	0.93	0.93	1.00	0.86	1.08
Nickel....	0.27	0.94	3.82	7.65	15.48	19.64	24.51	29.07	40.65

A shows three points of transformation, namely at  $775-765^\circ$ ,  $715-695^\circ$  and  $645-635^\circ$ , and C shows three points, at  $755-745^\circ$ ,  $695-685^\circ$ , and  $625-615^\circ$ . In the case of E, the second and third points coincide at  $645-635^\circ$ , whilst the first falls to  $565-550$ ; in G, the second and third points coincide at  $515-505^\circ$ , and the first point either disappears or coincides with the other two. As the proportion of nickel increases, the single point at which heat is developed during cooling becomes lower and lower; it is  $130-120^\circ$  in the case of J,  $85-65^\circ$  in the case of K, and the change is not complete even at the ordinary temperature in the case of L. M shows no appreciable development of heat, but N shows a point at  $380-340^\circ$ , from its position and feeble intensity, however, this seems to correspond with the known point of transformation of nickel.

The rate of cooling and the initial temperature have much less influence than in the case of hard steels or of alloys of iron with tungsten and chromium.

The appearance of magnetic properties seems to coincide with the second point. The alloys from A to L are strongly magnetic, but from G the magnetism decreases and M is almost non-magnetic. In N, however, the magnetism reappears. L is non-magnetic above  $50^\circ$ , but becomes magnetic between this temperature and  $0^\circ$ .

In J, K, and L the allotropic change is accompanied by a great increase in hardness, and the hardness corresponds with magnetic polarity as in the case of tempered steel. Both hardness and polarity seem to correspond with incomplete transformation.

C. H. B.

**Purification of Thorium Oxide.** By P. JANASCH (*Zeit. anorg. Chem.*, 6, 175).—The method of preparing pure thorium oxide, regarded as new by Böttger (this vol., ii, 238), had already been used by the author, Locke and Lesinsky (this vol., ii, 52).

C. F. B.

**Compounds of Thorium Oxide with Phosphoric and Vanadic acids.** By C. VOLCK (*Zeit. anorg. Chem.*, 6, 161—167).—By adding a rather dilute solution of orthophosphoric acid to a dilute solution of thorium chloride, a white flocculent precipitate is obtained soluble in acids; it has, when dried at  $100^\circ$ , the composition  $\text{ThO}_2 \cdot \text{P}_2\text{O}_5 + 2\text{H}_2\text{O}$  or  $\text{Th}(\text{HPO}_4)_2 + \text{H}_2\text{O}$ , and loses all its water at  $220^\circ$ . If



sodium phosphate is used to precipitate the thorium, the precipitate is always contaminated with sodium.

By adding an 8 per cent. solution of ammonium metavanadate to a dilute solution of thallium chloride, a greenish-yellow precipitate is obtained, soluble in acids; when dried at  $100^{\circ}$ , it has the composition  $\text{ThO}_2, \text{V}_2\text{O}_5 + 6\text{H}_2\text{O}$  or  $\text{Th}(\text{HVO}_4)_2 + 5\text{H}_2\text{O}$  C. F. B.

## Mineralogical Chemistry.

**Minerals of the Serpentine, Chlorite, and Mica Group.** By R. BRAUN (*Jahrb. f. Min.*, 1894, i, Mem., 205—244).—The author adversely criticises the method of investigation employed by F. W. Clarke and E. A. Schneider (Abstr., 1893, ii, 78) in their researches on the constitution of the natural silicates. He is of opinion that the hydrogen chloride gas used was not absolutely dry, and that that fact militated against the value of the theoretical views of Clarke and Schneider. His own theory is that the entire chlorite group is formed of several families existing in morphotropic relations. The individual families, whose representatives may be taken to be clinocllore, pennine, leuchtenbergite, and corundophilite, consist of several members existing in isomorphous relations. These members in isomorphous admixture invariably form minerals, a part of the magnesia being replaced by ferrous oxide, and of the alumina by ferric oxide, or by chromic oxide, &c. The micas, he believes, also form a morphotropic group. B. H. B.

**Meerschaum from Bosnia.** By M. KIŠPATIĆ (*Jahrb. f. Min.*, 1894, i, Ref., 443, from *Verhandl. k. k. geol. Reichsanst.*, 1893, 241—242).—At Ljubici-planina near Prnjavor, in Bosnia, meerschaum occurs with impure magnesite, and has the following composition.

MgO.	Fe <sub>2</sub> O <sub>3</sub> .	H <sub>2</sub> O.	Total.
25.87	2.59	10.47	100.02

B. H. B.

**Chemical Investigation of Topaz.** By P. JANNASCH and J. LOCKE (*Zeit. anorg. Chem.*, 6, 168—173).—This paper describes only the determination of the amount of water contained in crystals of topaz from different localities; this ranged from 0.80—2.69 per cent. A horizontal tube was used, with a bulb near one end, and a layer of dry lead oxide in the longer limb, which was connected with a calcium chloride tube. The powdered mineral was mixed with dry lead oxide, and the mixture placed in the bulb and fused, while a current of dry air was aspirated through the apparatus. The increase of weight of the calcium chloride tube gave the amount of water in the mineral.

C. F. B.

**Artificial Preparation of Beryl.** By H. TRAUBE (*Jahrb. f. Min.*, 1894, i, Mem., 275—276).—The author has obtained crystallised

beryl by a method similar to that employed by him in the preparation of zinc silicate. It consisted in precipitating the silicate in an amorphous state from an aqueous solution, and then melting it with boric anhydride at a high temperature. On adding sodium silicate to a solution containing 3 mols. of  $\text{BeSO}_4$  and 1 mol. of  $\text{Al}_2(\text{SO}_4)_3$ , a copious precipitate is obtained, having the composition  $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18} + x\text{H}_2\text{O}$ . Six grams of the carefully dried precipitate was mixed with 2.5 grams of boric anhydride in a platinum crucible, and heated for three days to a temperature of  $1700^\circ$ . The product was distinctly crystalline, colourless hexagonal tablets and prisms being detected. Analysis yielded

$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{BeO}$ .	Total.
67.38	18.61	13.48	99.47

Beryl is thus a metasilicate, as had previously been assumed. It may possibly be regarded as a double salt,  $3\text{BeSiO}_3 + \text{Al}_2\text{Si}_2\text{O}_7 = \text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ .  
B. H. B.

**Chemical Composition of Pyrope and other Garnets.** By C. v. JOHN (*Jahrb. f. Min.*, 1894, i, Ref., 436—437, from *Jahrb. k. k. geol. Reichsanst.*, 43, 53—62).—The author has analysed the typical pyrope from Meronitz (I), and from Triblitz (II), with the following results.

	$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Cr}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{FeO}$ .	$\text{MnO}$ .	$\text{CaO}$ .
I. 41.72	21.63	1.98	1.61	7.53	0.13	4.34	
II. 41.99	21.25	1.80	1.84	7.88	0.38	5.38	
		$\text{MgO}$ .	Total.	Sp. gr.			
		I. 21.42	100.36	3.70			
		II. 20.12	100.64	3.71			

He also gives the results of analyses of garnets from Australia, from India, from Olaphian, from Williamsburg, New York, and from Rez-bánya, in Hungary.  
B. H. B.

**Paramelaphyre.** By H. LORETZ (*Jahrb. f. Min.*, 1894, i, Ref., 459; from *Jahrb. preuss. geol. Landesanst.*, 1893, 129—137).—The eruptive rock, occurring at Gotteskopf, near Ilmenau, in Thuringia, described by E. E. Schmid, in 1881, as paramelaphyre, belongs to the porphyrite group. The holo-crystalline groundmass consists of plagioclase and orthoclase, with occasionally quartz. Magnetite, or titaniferous magnetite and apatite, are always present. In the groundmass, porphyrite crystals of biotite occur, with, more rarely, plagioclase and, in unaltered specimens, augite. Five analyses of the rock are given.  
B. H. B.

**Eklogites and Amphibole Rocks of Styria.** By J. A. IPPEN (*Jahrb. f. Min.*, 1894, i, Ref., 461—462; from *Mitt. naturw. Ver. f. Steiermark*, 1893, 56—97).—The eklogites of the Bacher mountains are essentially mixtures of omphacite and garnet, containing also horn-

blende, zoicite, zircon, and quartz. Carefully isolated omphacite gave on analysis the following results.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	Ignition.	Total.
I.	51.14	4.35	4.60	26.65	11.28	1.20	0.46	0.36	100.04
II.	51.28	4.28	5.21	18.51	16.58	1.73	0.85	1.20	99.64

I. Omphacite from the eklogite of St. Veit; sp. gr., 3.215. II. Omphacite from the eklogite of Tainach. B. H. B.

## Physiological Chemistry.

**Digestibility of Normal Oats and of Oats heated at 100°: Effect of Feeding with Oats on the Weight and Composition of Bones.** By H. WEINKE (*Landw. Versuchs-Stat.*, 43, 457—475).—It is frequently assumed that foods are rendered less digestible through heating, owing to the conversion of soluble albumin into the insoluble form, and the generally diminished digestibility of brown hay, pressed fodder, &c., as compared with that of normal food, is attributed to the high temperature to which such fodder has been exposed. Morgan (*Landw. Jahrb.*, 21, 69) showed that diffusive residues become considerably less digestible when heated at 125—130°, but that a temperature of 75° was without effect. Gabriel's results (*ibid.*, 38, 69) indicated that steam at 140° diminished the amount of digestible protein in lupins by about 20 per cent., and that the proteids in a substance which was originally almost entirely digested, lost one-eighth of their digestibility when heated for eight hours at 130—140° (compare Stutzer, *Bied. Centr.*, 1889, 209). The question is next considered from another side, namely, the effect of heat on the rate of digestion (compare Stutzer, *Landw. Versuchs-Stat.*, 40, 173, 311, and 317; *Abstr.*, 1891, 752; 1892, 1367). It is pointed out that an increase of the time required for digestion is not necessarily a disadvantage, and that substances may be too quickly digested. So that artificial digestion experiments are not sufficient, but must be supplemented by experiments with animals (compare Neumeister, *Lehrb. Physiol. Chem.*, 1, 305; Atwater, *Zeit. Biol.*, [2], 1888, 139; Chittenden and Cummins, *Abstr.*, 1885, 569; and Popoff, *Abstr.*, 1890, 1450).

In the author's experiments, two rabbits of the same litter were fed daily with oats (8 grams), the one with normal oats, the other with oats which had been heated at 100° successively in dry air and in moist air (48 hours). After 22 days, the feeding was reversed for a period of 18 days. During the first period, the weight of the rabbits remained almost constant, and both rabbits digested their food about equally well. The same results were obtained during the second period of the experiment, so that it may be assumed that the heated and normal oats have about the same value. It is,

however, suggested, that geese, &c., would digest less heated than normal corn, as the corn passes through the whole digesting canal in a few hours. In the second period, the digestion-coefficient for protein was less than in the first (with both rabbits). The feeding was continued for some days longer, until the rabbits began to leave portions uneaten, when they were killed and analysed. Two more rabbits of the same litter, which had been fed on hay and a little oats (and which had grown much more than those fed on hay alone) were also killed and analysed for comparison.

With the exception of the amount of fat in the bones, all the results (total amounts) obtained with the normally fed rabbits (hay and oats) are much higher than the others. This confirms the previous results, that oats without food giving an alkaline ash, has influence on the development of the bones. As regards the percentage results, it is shown, as in the previous experiments, that the bones, but not the teeth, are affected. The analysis of the bones indicates that there is more organic matter and less mineral in the bones of rabbits fed with oats alone than with those fed with hay and oats. In the ash itself, only the phosphoric and carbonic anhydrides vary to any extent, the phosphoric anhydride being slightly higher in the bones of rabbits fed with oats alone, and the carbonic anhydride being highest in the normally fed rabbits.

The rabbits were nine months old at the commencement of the experiment, and therefore completely developed (compare Wildt, *Landw. Versuchs-Stat.*, 15, 404). It is supposed that the continued feeding with oats alone caused a diminution of the skeleton, and especially of mineral matter. This is due, as previously stated, not to insufficient lime in the food, but chiefly to its acid nature.

N. H. M.

**Composition of the Skeletons of Animals of the Same Kind and Age, but of Different Weights.** By H. WEISKE (*Landw. Versuchs-Stat.*, 43, 475—480).—Three rabbits of the same litter were fed alike on hay and oats, and killed when they were 107 days old. They weighed 890, 1050, and 1480 grams respectively. The rabbits were analysed, and the results compared with those previously obtained with two other rabbits (also 107 days old), which had grown normally, and weighed 2020 and 1890 grams. The total weights of the skeletons and the percentage of live weight, and the composition of the skeletons, are given in tables.

The results show that in poorly developed rabbits the size and weight of the bones are less than in normally developed rabbits, and that the bones contain less minerals. As regards the teeth, the difference in weight is much less, and there is practically no difference in composition.

N. H. M.

**Influence of Subdivision of Food on Metabolism.** By C. ADRIAN (*Zeit. physiol. Chem.*, 19, 123—136; compare Abstr., 1893, ii, 383).—The present experiments, carried out on a dog, confirm on the whole the author's previous conclusions. The beneficial result of a subdivision of the food (flesh) into several meals is not due to the

increased consumption of proteid, as the total nitrogen in the excreta is the same as when the diet is all given in one large meal; but subdivision of the food lessens the amount of proteid which is decomposed into products of putrefaction, which are of no use in nutrition. The proteid absorbed as such is therefore increased. W. D. H.

**Metabolism in Italian Peasants.** By P. ALBERTONI and I. NOVI (*Pflüger's Archiv*, 56, 213—246).—The research was carried out on a man, woman, and boy belonging to an Italian peasant family, both in winter and summer. The results consist very largely of analytical tables of the food taken, with its heat value, and the output in urine and faeces.

Recent writers have urged that equilibrium is possible on smaller quantities of nitrogenous food than the older physiologists thought necessary. It is pointed out that individual idiosyncrasy must be taken into account before laying down a general rule, and this is emphasised by the fact that different results were obtained in the three subjects of experiment. W. D. H.

**Bile and Metabolism.** By C. VOLT (*Zeit. Biol.*, 30, 523—561).—This is a republication of experiments performed on two dogs many years ago.

The amount of bile and the time of maximum secretion were investigated under a large number of conditions—different diets, and so forth. Other excreta were in many cases analysed simultaneously. Full references are given to previous work on the same subject. The paper consists largely of elaborate tables and details, and general conclusions appear difficult to find. As previous observers state, most bile is secreted when the proteid in the food is abundant; the amount also appears to vary with the discharge of carbonic anhydride in the expired air. W. D. H.

**Sulphur in Human Muscle.** By H. SCHULZ (*Pflüger's Archiv*, 56, 203—212).—Previous analyses of the amount of sulphur in animal tissues (this vol., ii, 58) are here supplemented by experiments on human muscle. The average gives 1.1 per cent. of the dried, or 0.25 per cent. of the fresh tissue. Prolonged putrefaction causes little or no diminution in the amount. Traces only of this sulphur are contained as sulphate, but the amount of sulphate appears to be somewhat increased during the process of drying at 110°.

W. D. H.

**Estimation of the Volume of the Blood Corpuscles and Plasma.** By E. BIERNACKI (*Zeit. physiol. Chem.*, 19, 179—224).—Hamburger (*Abstr.*, 1893, ii, 426) has pointed out that so-called "physiological saline solution" is by no means an indifferent fluid to red blood corpuscles, and thus Bleibtren's method (*ibid.*, 331) for the estimation of the relationship between plasma and corpuscles is untrustworthy. The present communication points out another source of error in the use of the centrifugal machine.

Defibrinated blood yields more sediment than blood in which coagulation has been prevented by an oxalate. The amount of sedi-

ment is also increased by diluting it with "physiological saline solution." These differences appear to be due to the changes in the size of the corpuscles (shrinkage and swelling), and also as to whether or not they are collected into rouleaux.

The use of the centrifugal machine appears to exaggerate these differences, and in both defibrinated and oxalated blood (normal and pathological) the sediment is lessened as compared with specimens where the corpuscles are allowed to settle without the use of centrifugal force.

W. D. H.

**Fibrin and Fibrinogen.** By J. J. FREDERIKSE (*Zeit. physiol. Chem.*, 19, 143—163).—The view of blood coagulation urged by Pekelharing, Lilienfeld, and others, that fibrin originates by the interaction of fibrinogen and a calcium compound of nucleo-albumin, is urged.

The presence or absence of serum-globulin in such mixtures makes no difference in the amount of fibrin formed.

Hammarsten's statement that the fibrinogen molecule is split into fibrin or coagulated proteid and a soluble globulin by the action of heat or of fibrin ferment is confirmed. The same decomposition of the fibrinogen molecule is brought about by the action of dilute acetic acid.

W. D. H.

**Levulose in Diabetes.** By J. B. HAYCRAFT (*Zeit. physiol. Chem.*, 19, 137—141).—Patients with chronic diabetes can burn off 50 grams of levulose per diem. In some acute cases, a part of the levulose given is burnt off, a part is changed into dextrose, and a third part passes as such into the urine.

Rabbits can make glycogen from levulose, the glycogen so formed accumulating in the liver (compare Voit, *Abstr.*, 1892, 902).

W. D. H.

## Chemistry of Vegetable Physiology and Agriculture.

**Yeasts.** By P. HACTEFUILLÉ and A. PERREY (*Compt. rend.*, 118, 589—591).—The yeasts that produce the fermentation of the wines of Côtes de Nuits and Beaune may, with scarcely any exceptions, be divided into three groups. The first group consists of apiculated yeasts, which produce fermentation at the outset, and in some cases complete it. The second group consists of ellipsoidal yeasts more active than the first group. They complete the fermentation, and in the later stages completely displace the apiculated yeasts, probably because the latter lose their fecundity after a certain number of generations.

The third group consists of ellipsoidal yeasts, which in a neutral or slightly acid must behave rather after the manner of high yeasts, and acquire a rose or wine-red coloration. They are generally present, but seem to have little activity, although, in one case they

produced fermentation without the help of other yeasts; they show marked power of sporulation during their most active period, and even in a medium very favourable to nutrition, the sporulation takes place in the same manner as in the case of apiculated yeasts.

C. H. B.

**Proteolytic Ferments in Seedlings.** By R. NEUMEISTER (*Zeit. Biol.*, 30, 447—463).—Gorup-Besanez was the first to state that proteolytic and other ferments may be obtained from growing plants. This observation has been confirmed by some and contradicted by others. The cause of this discrepancy is to be found in the fact that different plants have been used by different observers, and that the methods employed are not calculated to settle the question definitely. The mere occurrence of albumoses and peptones in artificial digestive mixtures have in some instances been due to the hydrochloric acid used, and not to any ferment.

In the present experiments, advantage was taken of the circumstance that fibrin possesses the power of absorbing ferments from their solutions. Aqueous extracts of the seedlings were made; these were acid, and fresh fibrin was soaked in them; the fibrin was then removed, and placed in acid and alkaline mixtures, and the results observed, control experiments with acid and alkali alone being also performed.

Certain seedlings (barley, poppy, maize, wheat, rape) contain ferment which dissolves proteid. It is not formed in the earliest stages, but increases as the plant grows, and is very abundant when the latter has reached the height of 15—20 centimetres. This ferment works, like pepsin, only in acid liquids, but hydrochloric acid destroys it; a vegetable acid like oxalic acid is necessary. It was not found in lupins, vetches, peas, rye, or oats.

The plants during growth yield peptone, formed from pre-existing proteid, and there can be little doubt that the ferment described plays a part in its production, and that the peptone assists in the nutrition of the seedling.

W. D. H.

**Presence of Saponins in Plants, and their Determination.** By T. F. HANAUBEK (*Ann. Agron.*, 20, 62—63; from *Chem. Zeit.*, 16, Nos. 71, 72).—Authorities are not agreed as to the poisonous properties of corncockle seeds (*Agrostemma githago*). Recently, C. Kornauth and A. Arche have proved that pigs may be fattened on these seeds, which have for them the same nutritive value as barley. Other observers consider the seeds injurious, and maintain that where no harm occurs, it is because the saponins are in great part decomposed by the digestive juices.

The most important saponins, those characterised by Kobert, may be sought by the following microchemical reactions. Rosoll employed concentrated sulphuric acid. The root of saponaria and the bark of *Quillaja*, when treated with this reagent, show the contents of certain parenchyma tissue to be coloured yellow, red, and violet successively, but this reaction is also observed by concurrent action of the sulphuric acid on albumin, sugar, piperine, &c. A better plan is to use a mixture of equal parts sulphuric acid and alcohol.

Sometimes heat is necessary to produce the three colorations; a solution of ferric chloride thus produces a brown or blue-brown precipitate. The richer the drug in saprotoxins, the more does the blue colour predominate. This method has been tried with success on corncockle seeds, *Dianthus* seeds, fruits of *Sapindus*, *Saponaria*, and *Esculentus*, roots of *Saponaria*, *Senega*, *Polygala major*, and *Amaru*, and bark of *Quillaja*. In *Polygala* root the saponins are contained in the sub-peridermic cellular layers. In seeds of *Agrostemma*, and *Dianthus*, the embryo alone contains saponinis. J. M. H. M.

**Pentosans in Plants.** By G. DE CHALMOI (*Amer. Chem. J.*, 16, 218—229).—The author has made a number of determinations of pentosans in parts of plants of different ages and developments. The determinations were made by a slight modification of the method described by Flint and Tollens (*Abstr.*, 1893, ii, 52), the mixed pentosans being estimated as equivalent to twice the furfuraldehyde found. A large number of determinations were also made in various woods, and in the different aged rings of the same pieces of wood. The results show that the quantity of pentosans increases during the development of the plants. Thus the young leaves of the red oak contained 5.29 per cent. of pentosans, the fully developed leaves of the same plant 9.77; axil parts of corn cobs, of which the seed was in the earliest stage of development, contained 29.3 per cent. pentosans, similar ripe cobs from the same set of plants, 33.3 per cent.; and similar results were obtained in other cases. The determinations in woods showed that the quantity of pentosans is increased during the formation of wood, but does not alter thereafter. The author has not been able to trace any relation between the percentage of pentosans in wood, and the hardness, toughness, or durability of the latter. The wood of dicotyledonæ is, however, much richer in pentosans than that of coniferæ, the former containing from 17 to 25 per cent. of pentosans, the latter only about 10 per cent. or less. The author considers that the pentosans are not waste products, but accumulate during the whole life of the plant, and probably act, in part at least, as reserve substances. They also seem to be of importance in the formation of wood, being specially developed at this stage.

L. T. T.

**Occurrence of Trigonelline in Peas and Hemp-seed.** By E. SCHULZE and S. FRANKFURT (*Ber.*, 27, 769—770).—The undetermined base found in peas (*Abstr.*, 1891, 490) has now been identified with the trigonelline obtained by Jahns (*Abstr.*, 1886, 85) from *Trigonella* seed, and shown by him (*Abstr.*, 1888, 166) to be identical with Hantzsch's synthetically prepared methylbetaine of nicotinic acid (*Abstr.*, 1886, 369). It occurs, in small quantity only, both in green and dried peas (*Pisum sativum*), and in the seeds of hemp (*Cannabis sativa*). C. F. B.

**Drainage Waters from Arable Soils.** By P. P. DEHÉRAIN (*Ann. Agron.*, 20, 21—42).—The present paper records the results



obtained in 1893 with the sunk water-tight cases filled with natural soil and subsoil, as described in a former paper (Abstr., 1893, ii, 338).

The rainfall from November 12, 1892 to March 2, 1893, the period to which the present record refers, amounted to 143.4 mm., and the drainage water from the case under bare fallow measured 65.5 mm., or nearly half the rainfall. This drainage water was analysed on the following dates.

		Gram.	Kilos.
Dec. 8/92.	Nitric nitrogen per litre	0.183, per hectare	31.067
" 14/92.	" " "	0.157 "	21.195
Jan. 5/93.	" " "	0.011 "	0.960
" 20/93.	" " "	0.009 "	0.945
Feb. 8/93.	" " "	0.078 "	7.020
Mar. 2/93.	" " "	0.116 "	20.010

Thus, during January and February, nitrification was nearly at a standstill.

The author recognises that the loss of nitrates by drainage is in this first year of observation greatly exaggerated, the trituration and aëration of the soil, which occurred during the filling of the cases, having greatly promoted nitrification. The figures given by the various cases have, therefore, but a relative value. The general conclusions are:—

The losses by drainage are greater under bare fallow, the water percolating being both more abundant and richer in nitrates than in the case of soil under crop. In the latter case, the drains often do not run, and, when they do, the water is found nearly exhausted of nitrates by root absorption. The rotation most conducive to preservation of nitrate is that which keeps the land covered with green vegetation for the longest period. Thus potatoes or mangold grown for seed, allow more nitrate to be washed out in the autumn than mangolds grown for fodder. Wheat after mangolds, keeping the ground covered from April of one year to August of the next, allows little loss of nitrate; but in the eight months fallow before mangold sowing much nitrate escapes, unless a winter fallow crop be taken during this interval.

J. M. H. M.

**Pentosans in Soils.** By G. DE CHALMOT (*Amer. Chem. J.*, 16, 229).—The author has estimated the pentosans in three soils, with the following results.

Description of soil.	Humus.	Pentosans.	Pentosans in 100 parts humus.
Wood soil.....	23.42 per cent.	0.75 per cent.	3.2
Garden soil....	9.85 "	0.39 "	4.0
Poor sandy soil.	2.68 "	0.04 "	1.5

L. T. T.

**Farmyard Manure.** By G. C. WATSON (*Bied. Centr.*, 1894, 239—244).—In the winters 1891–2 and 1892–3, experiments were made to ascertain the relationship between the food consumed by domestic animals and the manure they produced. The animals employed for the purpose were sheep, cows, calves, pigs, and horses; the con-

stituents of the manure were estimated, and appraised; it was found, generally, that the consumption of water was not dependant on the amount of dry food consumed, but on the nitrogen contained in the fodder.

The manurial values of various fodders were found to be as follows. Maize meal, 5.664 dollars per ton; ensiled green maize, 1.24; clover hay, 7.554; cotton-seed meal, 26.16; linseed meal, 19.36; flesh meal, 35.668; oats, 6.70; skim milk, 2.108; timothy grass hay, 4.60; wheat bran, 12.301; wheat straw, 2.127. The values of the nitrogen, phosphoric acid, and potash in each fodder are also given.

E. W. P.

## Analytical Chemistry.

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### Phenomena of Oxidation and Chemical Properties of Gases.

By F. C. PHILLIPS (*Amer. Chem. J.*, 16, 163—187).—A contribution to the qualitative analysis of gases. The author has carried out a very large number of experiments on the phenomena of the oxidation of hydrogen and hydrocarbon gases by air in the presence of finely divided metals and other oxidising materials. The finely divided metal, coated on asbestos, was placed in a glass tube of  $\frac{1}{8}$ -inch bore, and the mixture of air and gas passed through the tube while the latter was gradually heated. The results obtained led to the following conclusions: (1.) The temperature of oxidation is mainly dependent on the solid substances with which the gas is in contact. (2.) Two phases are often, but not always, to be observed in the process of oxidation. As the temperature rises, a point is reached at which a minute and scarcely recognisable trace of carbonic anhydride appears; after this slow oxidation has continued for some time and gradually increased during a rise in temperature of 20°, or 30°, or even more, a sudden and intense reaction occurs; very often the first slow oxidation is not observed. (3.) The oxidation of a hydrocarbon by air, under conditions similar in all respects, does not always occur at the same temperature, the variation in initial oxidation temperature observed being sometimes considerable (in some of the experiments exceeding 50°). A variation in the proportion of inflammable gas and air does not seem materially to influence the oxidation temperature. (4.) The paraffins are the most stable towards air in presence of palladium; acetylene and carbonic oxide stand next in order; the olefines are the most easily oxidised. (5.) Of the members of the same homologous series, the lower are the more stable towards oxidising influences. (6.) Hydrogen stands alone among combustible gases in undergoing oxidation under the influence of palladium coated asbestos in the cold. (7.) Oxidation of gaseous hydrocarbons in excess of air involves the simultaneous formation of carbonic anhydride and water; no selective oxidation takes place, but oxidation is complete (that is, yields only carbonic

anhydride and water), even though a considerable portion of the hydrocarbon may escape unchanged. With insufficient air supply, the carbonic anhydride may be partly replaced by carbonic oxide. (8.) As regards oxidising power, the metals experimented with may be arranged in the following order, beginning with the most active: osmium, palladium, platinum and ruthenium, iridium, rhodium, gold. (9.) At a bright red heat, with excess of air, palladium asbestos causes oxidation of all hydrocarbons as efficiently as does ignited oxide of copper. (10.) The proportion of finely divided metal used upon the asbestos seems to be immaterial, palladium asbestos containing 2 per cent. of palladium, being nearly as efficient as that containing 30 per cent.

The author's results do *not* confirm Berliner's statements that (a) the catalytic action of each metal in the case of hydrogen begins at a fixed temperature and increases with rise of temperature; (b) that the oxidation temperature for platinum foil is about 270°, for copper 280°, for zinc 350°; and (c) that at constant temperature, the quantity of water formed is constant.

The following is a summary of the results obtained by the author with *palladium asbestos* and various gases, the figures given being the temperatures at which oxidation was observed to commence. Since, as mentioned above, this point varies considerably in different experiments carried out under apparently identical conditions, the lowest and highest initial oxidation temperatures observed are given:—Hydrogen, 20°, 55°; methane, 40½°, 41½°; ethane, 450°; propane 339°, 383°; isobutane, 220°, 250°; pentane, 170°, 210°; heptane, 270° 300°; ethylene, 180°, 224°; propylene, 170°, 200°; trimethylene, 260° 290°; isobutylene, 155°, 185°; acetylene, 339°, 359°; benzene, 250° 290°; alcohol vapour, 150°, 240°; carbon monoxide, 290°, 359°. xylene gave very varying results. From these results, it is apparent that Hempel's method of determining hydrogen in the presence of other gases, by adding oxygen and passing the mixture over very slightly warmed platinised or palladinised asbestos, should give good results, but that the method cannot be safely extended to the selective oxidation of other gases.

To determine, if possible, whether the different initial oxidation temperatures observed in different experiments might be due to lack of uniformity of condition in the metal-coated asbestos, experiments were made on the initial temperatures at which oxidation of combustible gases was affected by copper oxide, lead chromate, silver oxide, silver permanganate, and silver dichromate. The same variations were however observed, the initial oxidation temperatures of ethylene by silver dichromate varying, in different experiments, from 260° to 320°.

L. T. T.

**Phenomena of Oxidation and Chemical Properties of Gases.**  
By F. C. PHILLIPS (*Amer. Chem. J.*, 16, 255—277; compare preceding abstract).—Among the solutions treated with hydrogen, the following suffered change:—*Palladium chloride*; slowly, but completely reduced, cold, or at 100°. *Platinum chloride*; very slow, but complete reduction, cold, or at 100°. *Ammoniacal silver nitrate*; slowly reduced to metal. *Potassium ruthenate*; slowly reduced to

metal. *Potassium permanganate*; slowly reduced, whether in neutral, acid, or alkaline solution. *Ferric chloride*; traces of reduction to ferrous chloride after several hours at 100°.

Russell (Trans., 1874, 3) states that silver nitrate solution is reduced by hydrogen; the author confirms Pellet (this Journal, 1874, 867).

The temperatures of reduction of metallic chlorides by hydrogen were found to be as follows:—Anhydrous ruthenium chloride, 190°. Gold chloride, obtained by evaporating a solution of gold in aqua regia to dryness, 150°. Anhydrous rhodium chloride, 200°. Platinum chloride, obtained by evaporating a solution of the metal in aqua regia to dryness, below 80° (with evolution of water as well as hydrogen chloride). Silver chloride, 270—280°. Silver bromide, 330—360°. Silver iodide, 350—370°. Palladium chloride was reduced in the cold.

To apply the reduction of palladium chloride as a test for hydrogen, the gas to be tested is dried by calcium chloride and phosphoric anhydride, conducted through a tube to the bottom of a dry test tube containing 0.2 gram of palladium chloride, and then into silver nitrate solution. The test tube should be kept cold if oxygen or hydrocarbon be present; otherwise it should be heated at 40° or 50°. The precipitation of the silver as chloride will detect 0.05 per cent. of hydrogen in absence of oxygen; in testing for such small quantities, oxygen should be removed by contact with ferrous hydroxide.

Silver oxide is reduced by hydrogen at 100°; iodic acid is not reduced by hydrogen at 250°.

Methane was found to have very little reducing action; potassium ruthenate was slowly reduced to metal. Chlorine attacks methane only at temperatures above 100°; a mixture of methane and chlorine exposed over water to sunlight underwent no contraction in volume nor change of colour. Methane reduces silver chloride at 414°, and silver bromide at 439°; silver iodide volatilises without reduction.

Ethane and heptane are as stable as methane; propane and isobutane are somewhat more easily oxidised.

The following solutions suffered change when treated with ethylene:—*Palladium chloride*; quickly reduced; no carbonic anhydride formed; aldehyde produced. *Gold chloride*; very slow reduction; no carbonic anhydride. *Ruthenium chloride*; bleached after prolonged contact; no metal reduced. *Potassium permanganate*; rapidly reduced. *Osmic acid*; quickly reduced to metal. *Potassium ruthenate*; quickly reduced to metal. *Bromine water*; rapid but incomplete absorption. Ethylene liberates iodine from iodic acid at about 270°.

Propylene is slightly more stable than ethylene, especially towards gold chloride and potassium ruthenate solutions.

Isobutylene behaves like ethylene and propylene, but from mercurous nitrate precipitates a grey powder, consisting of (or changing into) mercury. It bleaches iodine in potassium iodide, and cerium dioxide in sulphuric acid; neither reaction is shown by ethylene or propylene.

Isobutylene, prepared from isobutylic alcohol, causes a white precipitate in ammoniacal silver nitrate solution; that from isobutylic iodide and potash does not.

Trimethylene gives reactions similar to those of the true olefines, but is decidedly more stable towards many reagents; thus, it does not reduce osmic acid, potassium permanganate, or gold chloride.

The most important reactions for distinguishing between olefines and carbon monoxide are the following:—(1.) The action of palladium chloride solution, which is reduced by carbonic oxide with formation of carbonic anhydride; the latter is not formed in the case of the olefines. (2.) Ammoniacal silver nitrate is not altered by olefines containing not more than 4 carbon atoms, but is reduced to silver and ammonium nitrite by carbonic oxide. (3.) Platinum chloride yields carbonic anhydride, but is not immediately reduced to metal by carbonic oxide. Ethylene produces no change. (4.) Rhodium chloride is slowly reduced by carbonic oxide, but is not altered by ethylene.

The author has failed to confirm Odling's statement that methane and carbonic oxide react at a high temperature to form water and acetylene.

A. G. B.

**Estimation of Water in Hygroscopic Substances.** By P. JANNASCH and J. LOCKE (*Zeit. anorg. Chem.*, 6, 174—175).—A U-tube of hard glass has one limb wide, the bend enlarged to a bulb, and the other limb narrower, and bent at right angles a little above the first bend; the laterally projecting end thus formed is ground into the end of a tube which contains dry lead oxide and is connected at its other end with a calcium chloride tube. The substance is pressed between filter-paper, and placed in the U-tube; dry air is then aspirated over it until its weight is constant, as determined by weighing the tube every five minutes, the ends being plugged during the weighing. Some dried lead oxide is then shaken down and mixed with the substance, and the mixture heated with a small flame, waved to and fro (so that the glass should not be attacked), whilst the water evolved is aspirated by a current of dry air into the calcium chloride tube, and there absorbed, and weighed. The method allows of the estimation of water in such substances as calcium and magnesium chlorides.

C. F. B.

**New Mode of Performing Schlöesing's Nitric acid Estimation.** By L. L. DE KONINCK (*Zeit. anal. Chem.*, 33, 200—205).—The decomposition is effected in a fractionating flask, whose side tube is bent upwards and connected with a small funnel by caoutchouc tubing, which is compressed by a screw clamp. The gas evolution tube, which is of small bore, is fitted to the neck of the flask by a rubber stopper. It is bent downwards at an acute angle, and is so long that its lower end is 75—80 cm. below the bend. At its lower end, it is formed into a T-piece, whose vertical tube, 6—7 cm. long and 7—9 mm. diameter, carries the graduated cylinder by means of a cork ring with radial notches on its upper surface. It rests on the bottom of a crystallising pan, containing as much mercury as will just close the end of the long tube, and the whole is plunged into a large vessel full of water. To make a determination, 40 c.c. of ferrous chloride (200 grams of iron to the litre), and 40 c.c. of hydrochloric

acid (1.1 sp. gr.) are placed in the flask, and the side tube is filled with acid up to the funnel. The liquid is then boiled until all air is expelled (the graduated cylinder being removed); the nitrate solution is placed in the funnel, and the lamp removed; the mercury rises in the tube, but can never reach the top. The nitrate is rinsed into the flask with hydrochloric acid without admitting air, and the nitric oxide is boiled out, leaving the apparatus ready for the next determination. It is well to adopt Grandean's suggestion to compare the volume of gas obtained in an analysis with that yielded by a known amount of a nitrate under the conditions as to time. The ferrous chloride in the flask suffices for as many estimations as will afford 800—900 c.c. of nitric oxide, or even for more if it is reduced again by adding stannous chloride. It is, however, absolutely necessary to avoid an excess of stannous chloride, and especially to leave none in the funnel and side tube.

M. J. S.

**Volumetric Estimation of Phosphoric acid.** By A. F. HOLLEMAN (*Zeit. anal. Chem.*, 33, 185—186).—See Abstr., 1893, ii, 490. From phosphates of the form  $M_2HPO_4$ , to which state acid solutions of phosphates may be brought by adding phenolphthalein and then an alkali until the change of colour just occurs, the phosphoric acid is completely precipitated by silver nitrate in presence of excess of sodium acetate. A known quantity of silver is added, and the excess is titrated by Volhard's method. A large excess is to be avoided, as the results are then less exact.

M. J. S.

**Estimation of Graphite in Pig-Iron.** By F. L. CROBAUGH (*J. Amer. Chem. Soc.*, 16, 104—108).—The author finds that very satisfactory results may be obtained by dissolving the metal in nitric acid (sp. gr. 1.135) and collecting the insoluble graphite and silica on two filters folded together, the outer one of which serves as a counterpoise. After drying at 100° and weighing, the inner filter is burnt and the weight of the silica ascertained. The graphite is then found by difference.

The silica may also be removed by treatment with nitric and hydrofluoric acids. Traces of carbon compounds may be got rid of by digesting the precipitate with dilute ammonia, or with a mixture of alcohol and ether.

L. DE K.

**Copper Analysis.** By J. S. DE BENNEVILLE (*J. Amer. Chem. Soc.*, 16, 66—67, and *Chem. News*, 69, 139—141).—The author has devised a method by which the great mass of the predominant constituents of copper alloys or pig-copper will remain in solution and the minor elements be concentrated in a small bulk, and corresponding ease in manipulation be obtained.

10 grams of copper is dissolved in nitric acid, any great excess of acid removed by evaporation, and ammonia added until the copper precipitate has redissolved. An excess of barium hydroxide is then added and the liquid filtered in about half an hour. The precipitate is well washed with dilute ammonia to remove any adhering copper salt. It may consist of lead, bismuth, tin, iron, manganese, and antimony; arsenic and phosphorus are not completely precipitated. After

adding potassium cyanide to the ammoniacal filtrate, any silver, zinc, and cadmium may be precipitated with hydrogen sulphide. The treatment of the two precipitates is left to the discretion of the operator. L. DE K.

**Analysis of Pig-Copper, Brass, and Bronze.** By J. S. DE BENNEVILLE (*J. Amer. Chem. Soc.*, 16, 133—140).—The author has studied the behaviour of tin towards nitric acid, and found that when the metal is evaporated with nitric acid for some time, it is completely converted into metastannic acid, which is insoluble in nitric acid, ammonia, and ammonium nitrate. If, when analysing a tin-copper alloy, the evaporation is pushed beyond a certain point, the oxide gets more or less contaminated with copper, manganese, iron, &c., which cannot be removed by washing with acid. If the tin is in excess, any phosphorus will be completely retained by the metastannic acid; any arsenic will also, for the greater part, enter into combination. These compounds are not properly decomposed by digesting with solution of sodium sulphide, but require fusion. Antimony behaves very similarly to tin, but its oxide is somewhat more soluble, particularly in dilute nitric acid. It does not retain phosphorus to the same extent as tin.

As tin oxide obtained from a copper alloy must always be purified, and as the separation of a small quantity of antimony from a large amount of copper, by means of sodium sulphide is, in practice, far from successful, the author strongly advises the concentration of the impurities in a small bulk by his ammonia-baryta process (see preceding abstract). L. DE K.

**Detection of Aluminium.** By G. NEUMANN (*Monatsh.*, 15, 53—54).—The presence of a minute quantity of aluminium in ordinary samples of potassium hydroxide and sodium hydroxide renders any method of detecting the metal, in which one of these reagents is employed, extremely unsatisfactory. The following is suggested as giving trustworthy results. The iron, chromium, and aluminium, precipitated as oxides by barium carbonate, are boiled with barium hydroxide solution, and the filtrate made slightly acid with hydrochloric acid and precipitated hot with sulphuric acid. The filtrate is concentrated and treated with ammonia, when the formation of a white zone shows the presence of aluminium. G. T. M.

**Estimation of Nickel in Nickel Steel.** By E. D. CAMPBELL (*J. Amer. Chem. Soc.*, 16, 96—102, and *Chem. News*, 69, 139—141).—The sample is dissolved in nitrohydrochloric acid, and the iron with traces of copper precipitated by means of sodium acetate and sodium phosphate. An aliquot part of the filtrate is precipitated, while boiling, with potassium hydroxide, the precipitate, which contains all the nickel, is well washed and dissolved in dilute hydrochloric acid, and the solution is then digested with granulated lead to remove the copper, and filtered. A solution of sodium phosphate and dilute ammonia is now added to precipitate the manganese and traces of lead, and the whole made up to a definite bulk; an aliquot part of the filtrate is

used for estimating the nickel, which may be done by titrating with potassium cyanide, using cupric ferrocyanide as indicator, or by electrolysis. The latter method is preferable when cobalt is suspected, as this will be deposited with the nickel.

L. DE K.

**Estimation of Nickel in Steel.** By J. WESTESON (*J. Amer. Chem. Soc.*, 16, 110—112).—1 gram of the sample is dissolved in 20 c.c. of sulphuric acid (sp. gr. 1.16) and the solution kept boiling for some time; the iron is now oxidised with nitric acid, the excess of which is then expelled by evaporation. The residue is dissolved in hot water, and after the bulk of the acid has been neutralised with sodium carbonate, the iron is precipitated as usual with sodium acetate, but it must be twice redissolved and reprecipitated. The united filtrates are concentrated to 400 c.c., mixed with 10 c.c. of strong ammonia, and boiled for a few minutes, so as to completely separate the manganese. (If ammonia be added to the liquid when cold, the manganese will not separate out, and will interfere with the estimation of the nickel.)

The nickel is now obtained by electrolytic deposition.

L. DE K.

**Estimation of Potassium Iodide and Sodium Acetate in the Presence of Complex Organic Mixtures.** By J. H. STEBBINS (*J. Amer. Chem. Soc.*, 16, 157—159).—The author recommends the following process for the estimation of potassium iodide and sodium acetate in samples of medicine:—10 c.c. of the sample is evaporated with 30 c.c. of 20 per cent. sulphuric acid in a large platinum dish, first on a steam bath, then on a sand bath, and finally charred; the carbon is then burnt off with the aid of ammonium nitrate. The ash which is left, consists of mixed potassium and sodium sulphates, from which the metals are calculated by the ordinary indirect analysis. The iodine is estimated by diluting 10 c.c. of the sample with water, filtering from any precipitate, and adding an acid solution of silver nitrate.

L. DE K.

**Detection of Salicylic acid in Food.** By K. P. Mc ELROY (*J. Amer. Chem. Soc.*, 16, 198—203).—The author tests for salicylic acid in canned vegetables as follows:—The contents of the can are pulped in a mortar, water and a little phosphoric acid are added, the mixture strained through a bag, and the liquid subjected to distillation. The first fractions hardly give any reaction with ferric chloride, as the acid has a tendency to accumulate in the later portions of the distillate, and the greater part of it is left in the distilling flask. The test with ferric chloride is safer than the reaction with Millon's reagent, which sometimes leads to erroneous results.

Hoorn has found that the distillation test is useless for beers, as in the process of fermentation certain phenol-like substances are formed which interfere with the reaction; but the author remarks that the presence of such compounds would also interfere with the shaking out process. [Hoorn has stated that six beers all gave salicylic acid reaction when distilled with a little sulphuric acid; all were free from salicylic acid when treated by the shaking out process.—Ab-



strator.] The author also uses a shaking out process:—The beer or wine is extracted with half its volume of ether, the latter evaporated to dryness and the residue taken up with warm water. The solution is then tested in the usual way with ferric chloride. Although this process extracts the full amount of salicylic acid, the reaction is often not quite so distinct as when the distillation process is used.

L. DE K.

**Estimation of Fat in Cheese.** By S. BONDZYŃSKI (*Zeit. anal. Chem.*, 33, 186—189).—The author employs for cheese the method suggested by Schmid for milk (Abstr., 1888, 1347), warming the weighed quantity of finely powdered cheese with 20 c.c. of 19 per cent. hydrochloric acid, until the casein is dissolved and the fused fat floats on the surface. 30 c.c. of ether is added, when the fat readily dissolves, and, either by the use of the centrifugal machine or by repose at 40°, the two layers separate sharply. After reading the volume of the ethereal solution, for which purpose the operation is performed in a flask with a calibrated neck, in the middle of which a bulb is blown, 20 c.c. of it is withdrawn and evaporated in a tared conical flask.

M. J. S.

**Estimation of Indigotin in Indigo.** By E. DONATH and R. STRASSER (*Zeit. angew. Chem.*, 1894, 11—13; 47—50).—After reviewing the chief methods in use for the estimation of indigotin, the authors finally recommend the following process:—1 gram of the powdered sample is mixed with four times its bulk of ignited pumicestone and exhausted in a Soxhlet-Szombathy extraction apparatus, first with warm, dilute hydrochloric acid, and then with a mixture of four parts of alcohol and one part of ether, to remove indigo-gluten and indigo-red. The residue is then extracted with about 30 c.c. of strong sulphuric acid for about two hours at 80°, the apparatus being suspended inside an air-bath. The solution is diluted with water to 1 litre, and 100 c.c. is diluted with 400 c.c. of water and titrated with potassium permanganate which has been carefully checked with pure indigotin under exactly the same conditions.

L. DE K.

**Estimation of Crude Fibre.** By V. STEIN (*Exper. Stat. Record*, 5, 613—614; from *Ugeskr. f. Landmand*, 39, 706—707).—The method for estimating crude fibre in cereals is as follows. The finely ground sample is freed from carbohydrates by treatment with malt decoction and subsequent washing with water; it is then treated with cold aqueous soda (1 per cent.), after which it is washed and treated with 1 per cent. hydrochloric acid, when it is allowed to settle. The residue is washed, transferred to a weighed filter (free from ash), washed with alcohol and ether, dried, and weighed. Nitrogen and ash are determined, and the amounts deducted. The results obtained are higher than those furnished by the Weende method. Samples of barley were found to contain 9.26 to 14.08 per cent. of crude fibre.

N. H. M.

## General and Physical Chemistry.

**Refraction Constants of Carbonyl Compounds.** By R. NASINI and F. ANDERLINI (*Gazzetta*, 24, i, 157—169).—The exceptionally high molecular refraction of nickel tetracarbonyl was attributed by Mond and Nasini (Abstr., 1891, 1322) to the octavalency of the nickel in this compound. Gladstone, however, is of opinion that the very high molecular refraction of ferropentacarbonyl (Abstr., 1893, ii, 254) is due to the peculiar arrangement of the carbonyl groups, and not to the presence of decavalent iron. The authors have measured the refraction constants of several carbonyl compounds, in order to ascertain whether the presence of a number of carbonyl groups in a molecule causes an abnormal increase in the molecular refraction similar to that observed by Zecchini in the case of the phenylamines (this vol., ii, 2).

The measurements were made for the ray  $H_\alpha$ , and the results are summarised in the following table.

Substance.	$P^{\mu_{H_\alpha} - 1} \cdot d$		$P^{\frac{\mu_{H_\alpha}^2 - 1}{(\mu_{H_\alpha}^2 + 2)d}}$	
	Observed.	Calculated.	Observed.	Calculated.
Quinone .....	48.27	46.80	27.98	27.28
Diacetyl .....	34.38	34.60	20.88	20.84
Diropionyl .....	49.79	49.80	29.96	29.96
Tetrachlorotetraketohexa- methylene .....	83.87	82.80	49.04	48.32
Dibromodichlorotetraketo- hexamethylene .....	95.57	93.8	55.23	54.18
Leuconic acid .....	67.16	66.00	39.78	38.60
Potassium croconate .....	86.48	—	48.91	—

The refraction constants of quinone, tetrachlorotetraketohexamethylene,  $\text{CCl}_2 < \begin{smallmatrix} \text{CO} \cdot \text{CO} \\ \text{CO} \cdot \text{CO} \end{smallmatrix} > \text{CCl}_2$ , and dibromodichlorotetraketohexamethylene were measured in benzene solution; leuconic acid and potassium croconate were examined in aqueous solution.

Leuconic acid combines with 5 mols. of water of crystallisation or combination; in aqueous solution it seems to possess the constitution  $\text{C}(\text{OH})_2 < \begin{smallmatrix} \text{C}(\text{OH})_2 \cdot \text{C}(\text{OH})_2 \\ \text{C}(\text{OH})_2 \cdot \text{C}(\text{OH})_2 \end{smallmatrix} >$ , since the molecular refractions calculated for this formula which are given in the above table agree closely with the observed values.

If the atomic refraction of potassium is taken as 8.1—the value deduced by Gladstone from the refraction of potassium salts—the

calculated molecular refraction of potassium croconate becomes 58.26 for the formula  $P \frac{\mu^2 - 1}{d}$ ; the atomic refraction of potassium must be taken as 22.5 for the simple formula and 12.40 for the  $\mu^2$  formula if the ordinary constant is assigned to the carbonyl groups. The authors attribute the abnormally high molecular refraction of this substance to the metal alone, since the measurements made on the other carbonyl compounds show that the presence of several carbonyl groups causes no abnormal increase in the molecular refraction. They do not deny that the anomalous results obtained with such compounds may be partly due to the measurements being sometimes made in solution, as supposed by Perkin (Trans., 1892, 800).

W. J. P.

**Refraction Constants of Furfurylic Alcohol and of Pyromucic acid and its Salts.** By G. GENNARI (*Gazzetta*, 24, i, 246—255; compare following abstract).—The author has determined the refraction constants of furfurylic alcohol and of pyromucic acid, (HPy), and several of its ethereal salts, for the lines  $H_\alpha$ ,  $H_\beta$ ,  $H_\gamma$ , and D. The results for the ray  $H_\alpha$  are summarised in the following table.

Substance.	Temp.	$P \frac{\mu_{H_\alpha}^2 - 1}{d}$	$P \frac{\mu_{H_\alpha}^2 - 1}{d(\mu_{H_\alpha}^2 + 2)}$	Atomic refraction of the furfurylic oxygen.	
				From $\mu$ .	From $\mu^2$ .
Furfurylic alcohol.	22.7°	42.2	24.75	2.6	0.97
HPy in $H_2O$ .....	22.6	44.02	26.18	2.82	2.14
EtOH ....	23.5	45.1	27.1	3.9	2.14
MePy .....	21.4	51.57	30.50	3.77	2.74
EtPy .....	20.8	59.4	35.29	3.14	1.90
PrPy .....	25.9	67.3	39.95	3.3	2.13
CHMe <sub>3</sub> ·Py .....	23.7	67.0	39.90	3.09	2.23
CMe <sub>3</sub> ·Py .....	27.5	—	44.6	3.44	2.18

The constants for pyromucic acid were determined in a 3.264 per cent. aqueous solution and in alcoholic solutions containing 19.522 and 25.06 per cent.; the values of the latter solution are considerably higher than those for the other two, which are given in the table. The other substances were examined in the pure state.

W. J. P.

**Refraction Constants of Oxygen, Sulphur, and Nitrogen in Heterocyclic Nuclei.** By R. NASINI and G. CARRARA (*Gazzetta*, 24, i, 256—290).—The authors have determined the refraction constants of a number of substances containing oxygen, sulphur, or nitrogen in a closed chain for the rays  $H_\alpha$ ,  $H_\beta$ ,  $H_\gamma$  and D. The results for the line  $H_\alpha$  are tabulated below.

Substance.	$t.^{\circ}$	$P^u - \frac{1}{d}$	$P \frac{\mu^2 - 1}{(\mu^2 + 2)d}$	Atomic refraction of the S, N, or O in the nucleus.	
				For $\mu$ .	For $\mu^2$ .
Furfuran .....	21.6	30.46	18.42	0.46	0.78
1 : 4-dimethylfurfuran....	17.7	46.75	23.01	1.55	1.25
Thiophen .....	25.1	41.40	24.18	11.40	6.54
1 : 4-dimethylthiophen ...	19.0	57.87	34.02	12.67	7.26
Pyrroline .....	21.0	35.09	21.39	3.79	1.86
1 : 4-dimethylpyrroline ...	19.8	50.83	29.90	4.83	2.10
Pyridine .....	12.4	40.72	23.87	4.42	2.73
Picoline .....	—	43.78	28.54	4.88	2.82
Quinoline .....	20.0	73.03	41.38	9.33	4.66
Isoquinoline .....	21.4	72.30	40.61	8.59	4.29
Piperidine .....	23.8	44.46	26.55	5.16	2.71
Coniine .....	23.0	67.86	40.51	5.76	2.99
2-Methylpyrazole .....	13.7	39.32	23.20	4.56	2.63
3 : 5-Dimethylpyrazole ..	25.7	48.02	28.39	5.11	2.94
1-Phenyl-3:4-dimethylpyrazole	19.4	92.12	53.09	5.96	3.10
1 : 4 : 5-Phenylmethyl-ethylpyrazole	22.0	101.63	53.53	6.91	3.54
1 : 4 : 3 : 5-Phenyldimethyl-ethylpyrazole	19.8	107.59	62.17	6.09	3.08

The values given for thiophen are calculated from Nasini and Scala's numbers (Abstr., 1887, 754). 3:5-Dimethylpyrazole was examined in an 11.209 per cent. benzene solution, but all the other compounds were examined in the pure state. The authors give a full discussion of the results, and consider that they support the conclusion that heterocyclic nuclei, like furfuran, pyrazole, &c., have a centric constitution similar to that which is by some attributed to benzene.

W. J. P.

**Constitution of Benzene. Refraction Constants and Molecular Volumes of Benzene Derivatives.** By J. W. BRÜHL (*J. pr. Chem.*, [2], 49, 201—294; *Ber.*, 27, 1065—1083). See this vol., i, 366.

**Spectra of Tin, Lead, Arsenic, Antimony, and Bismuth.** By H. KAYSER and C. RUNGE (*Ann. Phys. Chem.*, [2], 52, 93—118).—Of the elements of the fourth and fifth groups of the periodic system, only a few can be utilised for spectroscopic measurements. Germanium and the rare earths cannot be obtained in sufficient quantity or purity, carbon and silicon give only very few lines, and nitrogen and phosphorous no lines at all. The authors have therefore confined their observations to tin and lead in the fourth, and arsenic, antimony, and bismuth in the fifth group, the method employed being that described in former communications (Abstr., 1893, ii, 313).

Regularities similar to those observed in the spectra of other metals belonging to the same groups in the periodic system were not discovered, as the lines do not arrange themselves in series. There are, however, in all these spectra groups of lines which are repeated at least three times over, and between which there are constant differences in the vibration periods. H. C.

**Absorption Spectra of Cupric Bromide.** By P. SABATIER (*Compt. rend.*, 118, 1042—1045).—The author has examined the absorption spectra of solutions of copper bromide of different concentrations. Very concentrated solutions are extremely opaque and only admit of examination in layers of less than 1 mm. in thickness. The absorption spectra of such solutions is similar to that of solutions of the salt in alcohol. The absorption for these solutions is greatest in the green, and transmission is at a maximum in the red. As the solutions are diluted, the absorption in the green decreases and that in the red increases, until with very dilute solutions, absorption is at a maximum in the red and very slight in the green. H. C.

**Variation of Rotatory Power under the Influence of Temperature.** By A. LE BEL (*Compt. rend.*, 118, 916—918).—In order to avoid the probable presence of amylic alcohol, the author has prepared amylic isobutylic ether by the action of amylic chloride on sodium isobutoxide. The product thus obtained gives the following rotations in a column 200 mm. long.

$t^{\circ}$ .....	65°	15°	—42°
Rotation .....	+1° 28'	+1° 13'	+34'

Methylic lactate shows similar variations.

$t^{\circ}$ .....	100°	15°	—23°
Rotation .....	—4° 27'	—4° 2'	—2° 41'

All the compounds actually known to have variable rotatory power are compounds in which the asymmetrical carbon atom is united only with a single radicle containing an atom of oxygen united with another radicle. When, on the other hand, the asymmetrical carbon is united with two radicles of similar constitution, the variations of the rotatory power become almost *nil*. The rotatory power of methylic tartrate, for example, varies considerably with the temperature, whereas the rotatory power of methylic valeryl tartrate is practically constant, and the tetra-substituted ethereal salts of tartaric acid show no variations between 10° and 100°.

With a view to ascertain whether these variations are due to polymerisation or to changes in the internal structure of the molecules, Ramsay has determined the molecular weights of some of the compounds. Propyl glycol has a quadruple molecular weight at the ordinary temperature and a double molecular weight above 100°, but the rotatory power does not vary. Ethylic tartrate has a simple molecule at about 100°, but probably polymerises at low temperatures, when the rotatory power is much lower. Amylic isobutylic ether, however, has a simple molecule between —23° and +125°, and hence

the variations in rotatory power observed by the author and by Colson must be due to internal changes.

The facts can only be reasonably explained by assuming that the univalent unions become immobile at low temperatures, the molecule undergoing a kind of internal congelation. C. H. B.

**The Voltaic Chain.** By H. M. GOODWIN (*Zeit. physikal. Chem.*, 13, 577—656).—The author describes experiments made to test the validity of the law, that the potential difference between a metal and a solution depends on two constants—(1) a constant for the metal, (2) the cation concentration of the solution. Two cases are considered: when the solution is (i) that of a salt of the electrode, (ii) that of a sparingly soluble salt of the electrode in the presence of a soluble salt containing the same anion. The cause of the difference of potential is considered to be the emanation of ions from the metal into the solution until the ion pressure ( $p$ ), together with the electrostatic attraction of the metal for the ions  $-f(s)$ , is equal to a value  $P$ , constant for the metal. If the pressure  $p$  were originally greater than  $P$ , then the metallic ions would be deposited upon the metal until  $p - f(s) = P$ ;  $f(s)$  being in this case, of course, a repulsive force. Starting from this view, and equating the change of volume energy to that of electric energy, a value is obtained for the potential difference. As in the experiments, the E.M.F. of a cell with the same electrodes in different solutions was employed, the final equation is independent of  $P$ ;  $\text{E.M.F.} = \frac{RT}{ne\epsilon_0} \log_e \frac{p_1}{p_2}$ , where  $n$  is valency of metal,  $p_1$  and  $p_2$  the ion pressure, and  $\epsilon_0$  the electric equivalent 96,450 coulombs. A number of experiments follow with a chain of the nature of Case I—thallium, thallium chloride, and potassium nitrate, thallium chloride and potassium chloride, thallium—and the observed values agree well with these calculated by the formula developed, as is also the case when the salts of other metals are substituted for those of potassium. For the consideration of Case II, two chains of zinc, zinc chloride, mercurous chloride, mercury, with varying concentrations are opposed, and the observed and calculated values compared and found concordant. A number of changes are made which should theoretically have no effect on the E.M.F., such as substitution of bromides for chlorides, of silver and silver chloride for mercury and mercurous chloride, &c., and the results found as predicted. In the third portion of the communication, the author points out a method for the determination of the solubility of salts by the measurement of the E.M.F., and the results thus obtained are compared with those deduced by other methods. In the case of very insoluble salts, such as silver iodide, very different results are obtained by the different methods. The author considers the E.M.F. method the best when the solubility is below  $0.1 \times 10^{-4}$ , but for higher solubilities he regards the conductivity method as preferable. L. M. J.

**Copper Electrolysis in a Vacuum.** By W. GANNON (*Proc. Roy. Soc.*, 55, 66—83).—It is known that copper sulphate in solution does not conform rigorously to the simple form in which Faraday's

law of electrolysis is generally expressed, and it has been shown by Gray that the copper deposit is heavier the higher the current density and the lower the temperature, an explanation of this being given in the fact that copper dissolves to a very appreciable, although variable, amount in solutions of copper sulphate. According to Schuster, it is probably the oxygen of the air present in the solution that causes this chemical corrosion, and hence it was of interest to examine if any difference could be found between the weights of the deposits of two copper voltameters, one of which would be placed in a vacuum.

The author shows that with two copper voltameters containing freshly made neutral solution of copper sulphate, one of which is under reduced pressure, the other conditions being comparable, the copper deposit in the partial vacuum is higher than the deposit under the atmospheric pressure, but the percentage difference is not constant. If a little free sulphuric acid be added to the air solution, the percentage difference is more constant and higher than before. The addition of acid to both voltameters causes the percentage difference to be constant within experimental errors. Under this last condition, for current densities above 0.01 ampère per sq. cm. of active cathode, there is no practical difference between the two deposits, but for densities below 0.01 ampère per sq. cm., the vacuum deposit is very appreciably higher than the air deposit. A curve drawn representing the deposits obtained in a vacuum at different current densities is more regular than the air curves, and for densities below 0.01 ampère per sq. cm. is approximately a straight line.

H. C.

**Specific Heats and Latent Heats of Change of State of Solid Silver and Copper Sulphides and Selenides.** By M. BELIATI and S. LUSSANA (*Zeit. Kryst. Min.*, 23, 167—170; from *Atti Istit. Venet* (6), 7, 1051).—The remarkable anomalies in the electrical resistances of silver and copper selenides at different temperatures observed by the authors (*Atti Istit. Venet.* (6), 6, 189) have led them to investigate the rate of heating and cooling of the sulphides and selenides having the composition  $\text{Cu}_2\text{S}$ ,  $\text{Ag}_2\text{S}$ ,  $\text{Cu}_2\text{Se}$  and  $\text{Ag}_2\text{Se}$ ; it was thereby ascertained that these substances change into physically isomeric forms at definite temperatures. The change is, of course, accompanied by the development or absorption of heat, and the different physical modifications have different specific heats. The following table gives the heat of conversion,  $\lambda$ , in small, mean calories, and the two specific heats,  $\gamma$  just below the temperature of change  $t$ , and  $\gamma_1$  just above that temperature.

Substance.	$t$ .	$\lambda$ .	$\gamma$ .	$\gamma_1$ .
$\text{Cu}_2\text{Se}$ .....	110°	5.405	0.09805	0.08505
$\text{Ag}_2\text{Se}$ .....	133	5.641	0.06836	0.06843
$\text{Cu}_2\text{S}$ .....	103	5.630	0.13165	0.13330
$\text{Ag}_2\text{S}$ .....	175	3.843	0.08914	0.08804

The anomalous changes in the electrical resistances of these sub-

stances with temperature are thus explained by their peculiar behaviour towards heat; it is noteworthy that the electrical resistance and the specific heat of silver sulphide have constant values from  $79^{\circ}$  to  $175^{\circ}$ , the temperature at which change of state occurs. W. J. P.

**Fusibility of Mixtures of Salts.** By H. LE CHATELIER (*Compt. rend.*, 118, 800—804).—Mixtures of salts capable of forming double salts correspond with aqueous solutions of salts which form hydrates, and the author has previously shown that, in the case of the latter, each different compound, or each different state of the same compound, has a distinct curve of solubility. It follows that salts capable of forming a single definite compound will have a curve of fusibility consisting of three parts, one corresponding to the crystallisation of one of the salts, the second to the crystallisation of the other simple salt, and the third to the crystallisation of the double salt. The curves of the two single salts have the same form as if the double salt did not exist. The curve of the latter necessarily has a different form; its highest temperature of crystallisation is that which corresponds with its simple fusion, but this diminishes gradually when increasing quantities of one or other of the constituent salts are added, and tends, in the two cases, to approach absolute zero when the proportion of one or other of the single salts tends to become *nil*. The three curves, when taken in pairs, show a certain number of points of intersection which limit the available parts of the curves. The portions corresponding with a state of stable equilibrium are necessarily those which, for a given mixture, correspond with the highest temperature of crystallisation, in those cases, at least, where crystallisation is accompanied by a development of heat. The crystallisation of the double salt may take place between limits more or less extended, according to the relative position of the three curves, or even may not take place at all if its curve is entirely below those of the two simple salts. When part of the curve of the double salt is above that of the single salts, sometimes its summit (which corresponds with the melting point of the isolated double salt) will be on the stable part of the curve, and in this case the double salt can be fused without decomposing; if, however, the summit is outside the stable part of the curve, the fusion of the double salt is accompanied by precipitation of one of the constituents. The first case has been observed with some aqueous solutions, but is quite exceptional; the second case is that of the majority of saline hydrates which can be formed in aqueous solutions.

Curves are given for lithium potassium carbonate and for sodium phosphoborate respectively. The former contains equal equivalents of its constituents, is perfectly crystalline, and shows strong double refraction; the latter has no action on polarised light. The mixture of lithium and potassium carbonates shows supersaturation, which allows the curve of the double salt to be prolonged beyond that of potassium carbonate, a result analogous to that which would be obtained if a solution of sodium chloride could be cooled below the freezing point of its cryohydrate or eutectic mixture without solidification taking place.

C. H. B.



**An Improved Specific Gravity Bottle.** By H. LOUIS (*J. Soc. Chem. Ind.*, 1894, 322—323).—The new bottle differs from the ordinary type only in that the stopper is longer than usual, and is graduated, whilst a light glass cap is ground to fit accurately over the neck of the bottle, and thus to prevent the loss by evaporation that otherwise occurs during weighing, &c. It is filled in the usual way; the neck and stopper are then rapidly wiped dry, the cap is put on, and the body of the bottle dried. When weighing the bottle, any variation in the height of the column of liquid in the capillary tube must be read off on the graduations, which may be to any convenient scale; the author's graduations are  $\frac{1}{100}$  in. apart, corresponding with  $\frac{1}{100}$  grain of water. It is an easy matter to calibrate the tube and to make the necessary corrections. The capped bottle can be left for a long time without diminishing in weight through evaporation taking place.  
L. DE K.

**Rate of Diffusion of some Electrolytes in Alcohol.** By W. KAWALKI (*Ann. Phys. Chem.*, [2], 52, 166—190).—In this, the first portion of the author's communication, the method of experimenting, which is similar to that of Scheffer (*Abstr.*, 1888, 1144), is described. The application of Stefan's tables for calculating the diffusion coefficient is considered, and a modification given, which is better suited to the author's arrangement.  
H. C.

**Densities of Solutions of Soda and Potash.** By S. U. PICKERING (*Phil. Mag.*, [5], 37, 359—375).—The only existing data as to the densities of these solutions are very inaccurate and antiquated. In the present series, the mean experimental error is 0.0000063. The results with soda, which extend from 50 per cent. downwards and apply to a temperature of 15°, when plotted form a figure which is eminently complex, and shows eight breaks, several of which are very well marked. Of these, six occur at points corresponding with the hydrates already isolated by the author (*Trans.*, 1893, 890); the other two, which occur in weak solutions, correspond with the only two breaks found in the freezing point figure. A drawing, showing the above-mentioned breaks, attributes to the points an apparent error, agreeing almost absolutely with the known experimental error, whereas a drawing of a similar degree of complexity, placing the breaks elsewhere, gives an apparent error 6.6 times greater than the experimental error, and drawings obliterating every alternate break give errors 18 to 33 times greater. The results with potash form a simpler figure, and indicate somewhat uncertainly the existence of four breaks, one of which corresponds with the recently isolated tetrahydrate.  
S. U. P.

**Solubility of Mercuric Haloids in Carbon Bisulphide.** By H. ARCTOWSKI (*Zeit. anorg. Chem.*, 6, 260—267).—The solubility of mercuric chloride, bromide, and iodide in carbon bisulphide has been determined between -10° and +30°, and the results plotted against the temperature. The curve in each case consists of two straight lines, and indicates that the solubility increases with the temperature

at a constant rate until a certain point is reached, after which it increases at a greater, but still constant, rate. The solubility of the iodide is greater than that of the bromide, and increases with the temperature at a greater rate; the same is true of the bromide as compared with the chloride. The points of change of curvature of the three curves lie approximately on a straight line; the lower parts of the three curves intersect approximately in a point on the axis of temperatures, and they diverge almost at equal angles; and the straight line passing through the two points, given by special determinations of the solubility of the iodide at  $-21^{\circ}$  and at  $-76^{\circ}$ , intersects the axis of temperatures at a point almost coincident with the freezing point of the solvent.

Carbon bisulphide has no tendency to form molecular compounds with mercuric haloids, and it is thus impossible to account for the breaks of continuity in the above-mentioned curves in the same way as is done when the breaks in the curve of solubility of sulphuric acid in water are assumed to be due to the existence of definite hydrates, some of which it is possible to isolate. The author seems, indeed, to regard these hydrates as effects, rather than causes, of the phenomenon of solution. He looks on a solution as an ill-defined molecular compound between solvent and dissolved substance, and supposes that, when one thing does not dissolve in another, it is because the two substances are incapable of forming such compounds. The language of the paper is somewhat obscure on these points, probably due to its being a translation.

C. F. B.

**Velocity of Hydrolysis of Methylic Acetate by Water.** By J. J. VAN LAAR (*Zeit. physikal. Chem.*, 13, 736—756).—The value for the electrolytic dissociation of water, obtained by Wijs (*Abstr.*, 1893, ii, 364) from experiments on the hydrolysis of methylic acetate is considerably less than that obtained by Bredig, Walker, and Ostwald by other methods. The author first deduces an expression for the quantity of ethereal salt hydrolysed as a function of the time, and also for the point of least velocity, and compares the results with Wijs' experiments, and is of the opinion that the value obtained by Wijs,  $1.2 \times 10^{-7}$ , must be regarded as the most probable value and be accepted until more accurate determinations are made.

L. M. J.

**Velocity of Reaction between Ethylic Iodide and Sulphide.** By G. CARRARA (*Gazzetta*, 24, i, 170—179).—The reaction between ethylic iodide and ethylic sulphide is represented by the equation  $\text{Et}_2\text{S} + \text{EtI} = \text{SEt}_3\text{I}$ , triethylsulphine iodide being formed. The reaction is consequently of the second order, and should be represented by the equation  $\frac{dx}{dt} = C(A - x)(B - x)$ , where A and B are the molecular quantities of the interacting substances,  $x$  the amount of substance transformed during the time  $t$ , and C a constant. If the interacting materials are employed in equivalent proportion, A and B become equal, and, on integrating, it is seen that  $\frac{x}{t(A - x)}$  is constant.

The weighed mixture of ethylic sulphide and iodide in molecular proportion was placed in a closed tube, heated to the desired temperature for a known time, and then plunged into ice; the contents of the tube were filtered after adding ether, and the triethylsulphine iodide titrated in aqueous solution against standard silver nitrate. The constant given above was thus found to be 0.00013 at 41°, 0.00034 at 66°, and 0.00014 at 80°, the individual numbers for the two lower temperatures agreeing fairly well. The results obtained at 80° are not altogether satisfactory, owing to the partial decomposition of the triethylsulphine iodide at that temperature; at 100°, very little of the sulphine was obtained, only 0.65 per cent. of it remaining undecomposed after 990 minutes.

The presence of water considerably accelerates the action, and the above equation no longer holds, the system not being homogeneous. The author attributes this accelerating action to the greater stability possessed by the triethylsulphine iodide when partially dissociated in aqueous solution than when in the pure state. W. J. P.

**Effect of Neutral Solvents on the Velocity of Formation of Triethylsulphine Iodide.** By G. CARRARA (*Gazzetta*, 24, i, 180—189; compare preceding abstract).—The velocity of reaction between ethylic iodide and sulphide in solution changes as the solvent employed is changed. The following table shows the factors by which the velocity increases on the addition of various neutral organic solvents, the velocity coefficient 0.00034 at 66° (see preceding abstract) being taken as unity.

Solvent.	At 66°.	At 78°.	At 100°.
MeOH, 1 mol. ....	—	—	60.8
MeOH, 1 vol. ....	15.3	50.9	273.1
MeOH, 2 vols. ....	—	—	181.7
MeOH, 4 vols. ....	—	—	107.6
EtOH, 1 vol. ....	7.6	16.5	42.9
CH <sub>3</sub> Et-OH, 1 vol. .	4.7	12.9	21.7
CHMe <sub>2</sub> -OH, 1 vol. .	4.1	7.6	—
COMe <sub>2</sub> , 1 vol. ....	—	—	0.44

It will be seen from the table that alcohols increase the speed of the reaction, whilst acetone decreases it; the action does not proceed in presence of benzene or ether. The author agrees with Menschutkin that the cause of the different effects of various solvents on the velocity of reaction is not a physical one, but must be sought in the chemical constitution of the solvents themselves. W. J. P.

**Atomic Weights.** By J. THOMSEN (*Zeit. physikal. Chem.*, 13, 726—736).—The paper contains recalculations of the atomic weights as obtained from Stas' experiments and referred to O = 16. Silver is first calculated from five independent methods, and the mean value O<sub>2</sub>/Ag = 0.444733 obtained, whence Ag = 107.9299. From the value of silver, the numbers for chlorine, bromine, and iodine are

obtained, and from these, those for other elements, the results being contained in the accompanying table, together with Stas' own numbers and those recalculated by Van der Plaats.

	Stas.	Thom-en.	Van der Plaats.
Ag .....	107.930	107.9299	107.9244
Cl .....	35.457	35.4494	35.4565
Br. ....	79.952	79.9510	79.9548
I .....	126.850	126.8556	126.8494
S .....	32.074	32.0606	32.0590
Pb. ....	206.934	206.9042	206.9308
K .....	39.1425	39.1507	39.1403
Na .....	23.0455	23.0543	23.0443
Li .....	7.022	7.0307	7.0235
N .....	14.055	14.0396	14.0519

The author then points out that his numbers are preferable to those of Van der Plaats, inasmuch as they reproduce the original experimental numbers with a higher degree of accuracy, the average difference from the experimental ratios being only one-sixth of that obtained by the use of Van der Plaats' numbers, while further the differences are more uniformly distributed amongst the positive and negative signs. The value for hydrogen as calculated from the ratio  $\text{NH}_3/\text{HCl}$  (this vol., ii, 277) with the above values for nitrogen and chlorine becomes  $\text{H} = 0.9992$ .  
L. M. J.

**Apparatus for Distillation in a Vacuum.** By F. ANDERLINI (*Gazzetta*, 24, i, 190—191).—A somewhat complicated glass apparatus for use in distillation under reduced pressure is described and figured; it consists of a bell jar, into the neck of which is ground a stopper through which passes an adapter for taking the end of the condenser. The bell jar contains the vessels for collecting the distillate, and may be turned round in order to direct the separate fractions into the proper receptacles, the stopper remaining fixed.

The author employs Wurtz flasks having a small auxiliary bulb in the neck and a stem of some 50—60 cm. in length. Instead of filling the distilling flask with glass wool, as recommended by Angeli (this vol., ii, 39), the author prefers to stand a bundle of glass threads in the bulb, keeping them in place by a spiral of platinum wire contained in the neck of the flask.  
W. J. P.

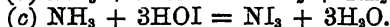
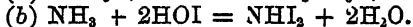
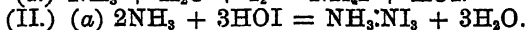
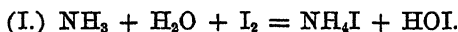
## Inorganic Chemistry.

**Atmospheric Hydrogen Peroxide.** By E. SCHÖNE (*Ber.*, 27, 1233—1235; compare this vol., ii, 88).—A reply to Nlosva's paper on this subject (this vol., ii, 277). Exception is taken to the statements that nitric peroxide is a constant constituent of air, and is the oxidising agent in it. The chief question at issue is one of fact, namely,

whether potassium iodide, starch, ferrous sulphate, and guaiacum diastase solutions are characteristic reagents for hydrogen peroxide, and although Ilosva denies this, the author has recently furnished detailed experimental proof in support of his assertion (*Zeit. anal. Chem.*, 1894, 137). In addition to hydrogen peroxide, organic peroxides, such as percarbonic acid, are probably present in the atmosphere, they are formed by plants in the presence of sunlight (compare Bach, this vol., ii, 186).

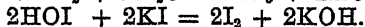
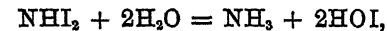
J. B. T.

**Chlorides and Iodides of Nitrogen.** By T. SELIVANOFF (*Ber.*, 27, 1012—1019).—The chlorides and iodides of nitrogen are considered by the author to be the amido-derivatives of hypochlorous and hypiodous acids. Iodide of nitrogen is most probably formed by the action of ammonia on hypiodous acid, which, along with ammonium iodide, is the first product of the reaction between ammonia and iodine.

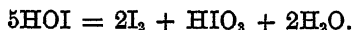


When a dilute solution of iodine is added to ammonia, the liquid remains clear and contains hypiodous acid. When a further quantity of iodine is added, iodide of nitrogen is precipitated, and the clear liquid then contains less hypiodous acid than before. On the other hand, iodide of nitrogen is soluble in a large amount of ammonia, yielding a solution which contains hypiodous acid, so that the equations (a), (b), and (c) given above are reversible. It is to this formation of hypiodous acid that many of the characteristic reactions of iodide of nitrogen must be referred, such as the liberation of oxygen from hydrogen peroxide, the formation of chloride of iodine by the action of hydrochloric acid, and the production of iodine derivatives from phenol. The accuracy of this view is further confirmed by the action of potassium iodide solution and of dilute acids on iodide of nitrogen.

Potassium iodide dissolves all the iodides of nitrogen more or less readily, and the solution formed contains ammonia, iodine, and caustic potash, the reaction being represented by the following equations:



Dilute acids, on the other hand, convert iodide of nitrogen into iodine and iodic acid, both of which are formed from hypiodous acid according to the equation



The change is usually accompanied by a certain amount of decomposition into iodine and nitrogen, but this can be wholly avoided if (1) a small amount of acid be employed, (2) sufficient water be present to dissolve the whole of the iodine formed, and (3) the iodide of nitrogen be in the form of a very fine powder.

In the light of the formation of the iodides of nitrogen by the

action of ammonia on hypiodous acid, the author proposes the following names for the these substances:  $\text{NH}_3\cdot\text{NI}_3$ , *sesqui-iodylamide*;  $\text{NHI}_2$ , *di-iodylamide*;  $\text{NI}_3$ , *tri-iodylamide*.

The chlorides of nitrogen are probably always formed in a similar manner to the iodides by the action of ammonia on hypochlorous acid, a reaction which has been used for their preparation. When chloride of nitrogen is treated with dilute sulphuric acid, it is partially dissolved, the solution giving the reactions of hypochlorous acid; the accumulation of hypochlorous acid, however, prevents any further decomposition of the chloride, and the greater part of it therefore remains unchanged. When hydrochloric acid is employed, on the other hand, the hypochlorous acid is decomposed with formation of chlorine as fast as it is formed, and the entire amount of chloride of nitrogen is rapidly decomposed. In the same manner, chloride of nitrogen is completely decomposed by a solution of succinimide, which reacts with the hypochlorous acid to form chlorylsuccinimide (Abstr., 1893, i, 192).

Other interesting reactions of chloride of nitrogen are that solid iodine produces an explosion, whilst a dilute solution yields iodic acid, and that it undergoes an energetic reaction with potassium iodide, iodine being liberated.

A. H.

**Preparation of Free Hydroxylamine.** By J. W. BRÜHL (*Ber.*, 27, 1347).—Polemical. A rejoinder to Lobry de Bruyn (this vol., ii, 278).

**Phosphoric Anhydride.** By H. BILTZ (*Ber.*, 27, 1257—1264).—Ammonia reacts energetically with phosphoric anhydride at ordinary temperatures, forming a dark reddish-brown mass consisting chiefly of phosphamic acid. On treatment with water, hydrogen phosphide is evolved, and yellow phosphorus (0.05 per cent.) is formed, together with a reddish, flocculent substance (0.1—0.2 per cent.). This substance is not red phosphorus, as Schiff stated, but the suboxide,  $\text{P}_4\text{O}$ . By the action of potash, hydrogen phosphide is formed; in presence of moisture, white vapours are evolved, and on warming with sulphuric acid, phosphoric acid and sulphurous anhydride are formed. Phosphorus suboxide is formed in small quantity by heating phosphoric anhydride at  $250^\circ$  either in a vacuum or in a current of air, carbonic anhydride, hydrogen, oxygen, or steam; the maximum yield is 0.06 per cent.; it is also formed in traces by dissolving the anhydride in water or soda. The formation of the suboxide is conditioned by a high temperature, and the presence of phosphorus oxide in the phosphoric anhydride, since it is not formed by the action on the latter of water in large excess, of ammonia at low temperatures, or in any circumstances from water or ammonia, and anhydride which has been purified by sublimation over platinum black in a current of oxygen. A quantity of suboxide was formed from a portion of anhydride which had been heated at  $230^\circ$  during several hours, so that either this treatment was insufficient to remove all the phosphorus oxide (b. p.  $173^\circ$ ), or the commercial anhydride contains small quantities of other lower oxides of phosphorus.

J. B. T.

**The Yellow Modification of Arsenic.** By J. W. RETZGERS (*Zeit. anorg. Chem.*, 6, 317—320).—In his previous paper (Abstr., 1893, ii, 570) the author had neglected to notice Schuller's work (*Math. u. naturw. Ber. aus Ungarn* (1889), 6, 94), to which he now draws attention. Schuller sublimed pure arsenic in a vacuum, and obtained a yellow sublimate of arsenic, characterised by its extreme volatility and by its instability. He further calls attention to the parallel series of modifications of phosphorus and arsenic.

## Phosphorus.

- (a.) Colourless, regular.
- (b.) Light-red (? regular).
- (c.) Dark-red to opaque, hexagonal, "metallic phosphorus."

## Arsenic.

- (a.) Yellow.
- (b.) Black (? regular).
- (c.) Silver-white, hexagonal.

C. F. B.

**Potassium Arsenite Sulphate.** By A. STAVENHAGEN (*Zeit. angew. Chem.*, 1894, 165—166).—The author, some time ago, investigated compounds of arsenic trioxide with sulphuric anhydride (Abstr., 1893, ii, 459), and has now succeeded in preparing a double salt of potassium sulphate with potassium arsenite. 21.8 grams of potassium sulphate and 3 grams of potassium ortharsenite were dissolved in 85 c.c. of water, evaporated to the crystallising point, and slowly left to crystallise. The double salt separated as small, lustrous prisms, showing hexagonal forms when viewed under the microscope. Analysis proved its formula to be  $K_4AsO_3 \cdot 10K_2SO_4$ . L. DE K.

**Complex Acids: Condensation Products of Alkali Phosphates or Arsenates with Chromates and Sulphates, and of Nitrates with Sulphates.** By C. FRIEDHEIM (*Zeit. anorg. Chem.*, 6, 273—302).—It has been shown, in the previous work on complex inorganic acids (Abstr., 1893, ii, 283), that these acids are not, as hitherto supposed, molecular compounds, but that they form complex molecules of definite atomic structure. For instance, the compound mentioned below as obtained from potassium dihydrogen phosphate and sulphuric acid, is to be regarded, not as  $2K_2O \cdot P_2O_5 \cdot 2SO_3 \cdot 3H_2O$ , or as  $KHSO_4 \cdot KH_2PO_4 + 2H_2O$ , but as  $OH \cdot PO(OK) \cdot O \cdot SO_3 \cdot OK + H_2O$ . The evidence of this is manifold; these compounds cannot be obtained directly by crystallising a mixture of their constituents from water; they cannot themselves be recrystallised from water without undergoing decomposition; and the water, of crystallisation or of constitution, which they contain, is always lost either at a higher or at a lower temperature than is the case with the substances of which they might be regarded as molecular compounds; never at the same temperature.

These complex molecules always contain two acids corresponding with oxides of the types  $R_2O_3$  and  $RO_3$  respectively; and they are only formed when the latter acid is one capable of condensing with itself; as, for example, chromic acid, of which potassium dichromate,  $OK \cdot CrO_3 \cdot O \cdot CrO_3 \cdot OK$ , is a condensation product. The more nearly this acid approaches a base in character, the larger is the number of such condensation products which it will form, and the larger, too,

the number of its "complex" compounds. Thus, molybdic and tungstic acids are known to form many such compounds; chromic and sulphuric acids, which will condense, but not so readily, are now shown also to form complex compounds, but these are fewer in number. It is further shown that the acid oxide,  $R_2O_5$ , need not necessarily be  $V_2O_5$ ,  $P_2O_5$ , or  $As_2O_5$ ; it may even be  $N_2O_5$ . To conclude, in the author's words, "the composition of the so-called complex compounds, derived from acids  $R_2O_5$  and  $RO_3$ , is closely dependent on that of the acid salts which the two acids are capable of forming, and on the more or less basic character of the trioxide."

A list is given below of the compounds described in the paper. The formulæ of these is contained in the middle column; in that to the left is given the constitution of the aqueous solution from which they were crystallised, and when some substance crystallised out of the solution before the complex compound in question, the formula of that substance is given in the right-hand column.

$\left. \begin{array}{l} \text{KH}_2\text{AsO}_4 \cdot \text{CrO}_3 \\ \text{As}_2\text{O}_5 : \text{K}_2\text{Cr}_2\text{O}_7 \\ \text{As}_2\text{O}_5 : (\text{NH}_4)_2\text{Cr}_2\text{O}_7 \end{array} \right\}$	$\text{OH} \cdot \text{AsO}(\text{OK}) \cdot \text{O} \cdot \text{CrO}_2 \cdot \text{O} \cdot \text{CrO}_2 \cdot \text{OK}$	$\text{K}_2\text{Cr}_2\text{O}_7$
$\left. \begin{array}{l} \text{NH}_4\text{H}_2\text{AsO}_4 \quad \text{CrO}_3 \end{array} \right\}$	$\text{OH} \cdot \text{AsO}(\text{ONH}_4) \cdot \text{O} \cdot \text{CrO}_2 \cdot \text{O} \cdot \text{CrO}_2 \cdot \text{ONH}_4$	$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$
$\left. \begin{array}{l} \text{P}_2\text{O}_5 : \text{K}_2\text{Cr}_2\text{O}_7 \\ 1 \cdot 5\text{P}_2\text{O}_5 : \text{K}_2\text{Cr}_2\text{O}_7 \\ \text{P}_2\text{O}_5 : (\text{NH}_4)_2\text{Cr}_2\text{O}_7 \end{array} \right\}$	$\text{AsO}(\text{ONH}_4)(\text{O} \cdot \text{CrO}_2 \cdot \text{O} \cdot \text{CrO}_2 \cdot \text{ONH}_4)_2$ $\text{OH} \cdot \text{PO}(\text{OK}) \cdot \text{O} \cdot \text{CrO}_2 \cdot \text{O} \cdot \text{CrO}_2 \cdot \text{OK}$	$\text{K}_2\text{Cr}_2\text{O}_7$
$\left. \begin{array}{l} \text{NH}_4\text{H}_2\text{PO}_4 : \text{CrO}_3 \\ 2\text{KH}_2\text{AsO}_4 : \text{H}_2\text{SO}_4 \\ \text{KH}_2\text{AsO}_4 : \text{H}_2\text{SO}_4 \\ 2\text{NaH}_2\text{AsO}_4 : \text{H}_2\text{SO}_4 \\ \text{NaH}_2\text{AsO}_4 : \text{H}_2\text{SO}_4 \end{array} \right\}$	$\text{PO}(\text{ONH}_4)(\text{O} \cdot \text{CrO}_2 \cdot \text{O} \cdot \text{CrO}_2 \cdot \text{ONH}_4)_2$ $\text{OH} \cdot \text{AsO}(\text{OK}) \cdot \text{O} \cdot \text{SO}_2 \cdot \text{OK} + \text{H}_2\text{O}$ $\text{As}(\text{OK})(\text{O} \cdot \text{SO}_2 \cdot \text{OK})_4 + 3\text{H}_2\text{O}$	$\text{KHSO}_4$
$\left. \begin{array}{l} 2\text{NH}_4\text{H}_2\text{AsO}_4 : \text{H}_2\text{SO}_4 \\ \text{NH}_4\text{H}_2\text{AsO}_4 : \text{H}_2\text{SO}_4 \\ 2\text{KH}_2\text{PO}_4 : \text{H}_2\text{SO}_4 \\ 2\text{H}_2\text{PO}_4 : \text{K}_2\text{SO}_4 \end{array} \right\}$	$\text{OH} \cdot \text{AsO}(\text{ONa}) \cdot \text{O} \cdot \text{SO}_2 \cdot \text{ONa} + \text{H}_2\text{O}$ $\text{OH} \cdot \text{AsO}(\text{ONH}_4) \cdot \text{O} \cdot \text{SO}_2 \cdot \text{ONH}_4 + \text{H}_2\text{O}$ $\text{—}$	$\text{NaHSO}_4$ $(\text{NH}_4\text{HSCo}_4)$ $(\text{NH}_4\text{HSO}_4)$
$\left. \begin{array}{l} 2\text{NH}_4\text{H}_2\text{PO}_4 : \text{H}_2\text{SO}_4 \\ 2\text{KNO}_3 : \text{H}_2\text{SO}_4 \\ 2\text{NH}_4\text{NO}_3 : \text{H}_2\text{SO}_4 \end{array} \right\}$	$\text{OH} \cdot \text{PO}(\text{OK}) \cdot \text{O} \cdot \text{SO}_2 \cdot \text{OK} + \text{H}_2\text{O}$ $\text{OH} \cdot \text{PO}(\text{ONH}_4) \cdot \text{O} \cdot \text{SO}_2 \cdot \text{ONH}_4 + \text{H}_2\text{O}$ $\text{OH} \cdot \text{NO}(\text{OK}) \cdot \text{O} \cdot \text{SO}_2 \cdot \text{OK}$ $\text{OH} \cdot \text{NO}(\text{ONH}_4) \cdot \text{O} \cdot \text{SO}_2 \cdot \text{ONH}_4$	

C. F. B.

**Some Properties of Carbon Bisulphide.** By H. ARCTOWSKI (*Zeit. anorg. Chem.*, 6, 255—259).—At 130° mercuric chloride is fairly soluble in carbon bisulphide. At 8°, 100 parts of saturated carbon bisulphide solutions of mercuric chloride, bromide, and iodide contain 0.030, 0.122, and 0.238 parts of the respective salts. The following salts, KCl, KBr, KI, KNO<sub>3</sub>, K<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SbO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>3</sub>PO<sub>4</sub>, NH<sub>4</sub>Cl, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, AgNO<sub>3</sub>, AgI, MgCl<sub>2</sub>, MgSO<sub>4</sub>, CdI<sub>2</sub>, SnCl<sub>2</sub>, PbCl<sub>2</sub>, PbI<sub>2</sub>, Pb(NO<sub>3</sub>)<sub>2</sub>, CuI, HgCl<sub>2</sub>, ZnCl<sub>2</sub>, Cr<sub>2</sub>Cl<sub>3</sub>, Al<sub>2</sub>Cl<sub>3</sub> are insoluble, and HgI<sub>2</sub> and Fe<sub>2</sub>Cl<sub>6</sub> only very slightly soluble. Boiling carbon bisulphide, however, dissolves HgNO<sub>3</sub>, and also Pb(NO<sub>3</sub>)<sub>2</sub> to a slight extent.

Sidot's method of purifying carbon bisulphide is the best. The liquid is shaken with mercury until all marked ethereal odour has



disappeared, decanted, and slowly distilled. It is best to purify only small quantities at a time, and these immediately before use. The pure liquid boils at  $46.27^{\circ}$ , under 756 mm. pressure, and is almost free from smell. It remains pure when kept at the ordinary temperature in the absence of light, air, and moisture, but under other circumstances very readily undergoes slight decomposition.

C. F. B.

**Sodium Peroxide.** By T. POLECK (*Ber.*, 27, 1051—1053).—The chemical behaviour of sodium peroxide is quite analogous to, but much more energetic than, that of the peroxide of hydrogen or barium. It reduces salts of gold, silver, and mercury to the metallic state, with evolution of oxygen; platinic chloride solution is only reduced after decomposition of the hydrogen platinochloride by the addition of a silver salt. Sodium peroxide precipitates ferric hydroxide from ferrous and ferric solutions, and manganese peroxide and cobalt oxide from manganese and cobalt solutions respectively; it reduces permanganic acid to manganese peroxide, and oxidises chromous oxide to chromic anhydride. With uranium salts, it yields sodium peruranate,  $\text{Na}_4\text{U}_2\text{O}_8 + 8\text{H}_2\text{O}$ , which is precipitated by the addition of alcohol, and sets free chlorine from hydrochloric acid; on prolonged boiling, the solution of the peruranate becomes red, evolves oxygen, and then deposits sodium uranate. Sodium peroxide rapidly oxidises the hydroxide and salts of bismuth to bismuthic acid, and immediately reduces potassium ferricyanide to the ferrocyanide; the latter reaction forms the basis of Kassner's method for estimating the peroxide (*Arch. Pharm.*, 228, 182, 432). Iron and chromium, or manganese and chromium, may be separated and estimated by the use of sodium peroxide, since the chromium is oxidised to chromic anhydride, whilst the other metals are precipitated. Tin, antimony, and arsenic may also be separated by precipitating as sulphides with ammonium sulphide, evaporating off the excess of the latter, and oxidising the dissolved sulphides with sodium peroxide; the oxides of the metals may then be separated in the ordinary way. The oxidised product may be at once tested for arsenic by Marsh's method, which would be impossible if nitric acid had been the oxidising agent employed. The fusion of silicates and metallic minerals with a mixture of sodium carbonate and peroxide would lead to an excellent method for their analysis, if crucibles of porcelain, platinum, nickel, and silver were not considerably corroded during the process.

Sodium metaplumbate is formed by the action of the peroxide on lead oxide, in presence of water; the orthoplumbate could not be prepared. Iodine combines with the peroxide on heating, with formation of sodium periodate. It would seem that the peroxide might advantageously be used as an oxidising agent for organic substances; it does not act on alcohol, but ether inflames on contact with it.

W. J. P.

*Note.*—No reference is made to Fairley's work on sodium peruranate (this Journal, 1877, i, 139). According to the latter, the formula of the salt is  $\text{Na}_4\text{UO}_8 \cdot 8\text{H}_2\text{O}$ .—[EDITORS.]

**Sodium Nitride.** By L. ZEHNDER (*Ann. Phys. Chem.*, [2], 52, 56—66).—The author has observed that when sodium is introduced electrolytically into glass tubes, such as are used for illustrating Hertz experiments, a portion of the deposit is reddish-brown in colour, and in appearance closely resembles metallic copper. This is found to be due to the combination of nitrogen with part of the sodium, and probable formation of the compound,  $\text{NNa}_3$ . H. C.

**Action of Water on Bicalcium Phosphate.** By A. JOLY and E. SOREL (*Compt. rend.*, 118, 738—741).—When crystals of hydrated bicalcium phosphate are thrown into boiling water they become opaque, and the liquid, which is acid to litmus but neutral to methyl-orange, contains monocalcium phosphate, whilst the insoluble matter, which has become amorphous, is almost pure tricalcium phosphate. The conversion into tricalcium phosphate is made complete by repeated treatment with boiling water.

If with a constant quantity of water the proportion of bicalcium phosphate to water is less than 10 grams per litre, the product seems to be a mixture, but it has not yet been completely examined; if the proportion of bicalcium phosphate is higher than 10 grams per litre, the ratio of calcium oxide to phosphoric anhydride diminishes as the proportion of salt to water increases, and the product is at first a mixture, but when the proportion of salt exceeds 15 grams per litre the product is completely crystalline, and seems to consist of the compound  $\text{Ca}_3(\text{PO}_4)_2 \cdot 4\text{Ca}_2\text{H}_2(\text{PO}_4)_2 + 2\text{H}_2\text{O}$ . The conversion of hydrated bicalcium phosphate into the anhydrous salt in presence of boiling water, is due to a chemical change in which tricalcium phosphate is an intermediate product. The complete change is rapid and complete only when the liquid is acid; the salt is obtained in a state of purity by adding calcium chloride to a boiling solution of disodium phosphate and monosodium phosphate. In order to obtain pure hydrated bicalcium phosphate, the liquid must likewise be acid. When calcium chloride is precipitated by disodium phosphate, the product is at first gelatinous tricalcium phosphate, whilst the liquid is acid both to litmus and to methyl-orange. Gradually, however, the precipitate is converted by the action of the acid liquid into crystallised bicalcium phosphate, the change being more rapid the more concentrated the solution, but the addition of a further quantity of acid is necessary to make the change quite complete.

C. H. B.

**Artificial Preparation of the Barium and Strontium Analogues of Apatite and of Basic-slag.** By C. v. WOYCZYNSKI (*Zeit. anorg. Chem.*, 6, 310—311).—By oxidising 1.88 grams of phosphorus with nitric acid, adding 26.24 grams of barium nitrate and 0.7 gram of 57 per cent. hydrofluoric acid, and carefully neutralising with ammonia, a granular precipitate was obtained, which, when recrystallised, showed the characteristic forms of apatite, and had the composition  $3\text{Ba}_3(\text{PO}_4)_2 \cdot \text{BaF}_2$ . An analogous strontium compound was prepared.

By fusing 14 grams of barium hydroxide with 4 grams of sodium hydroxide, as far as possible in the absence of air, and adding 5 grams

of sodium phosphate, the barium analogue  $\text{Ba}_3(\text{PO}_4)_2 \cdot \text{BaO}$ , of basic slag was obtained in small, quadratic tables. The strontium analogue can be obtained in a similar way. C. F. B.

**Colloidal Zinc Sulphide.** By P. DONNINI (*Gazzetta*, 24, i, 219—222).—It is well known that precipitated zinc sulphide may be washed with ammonium chloride solution without any turbidity of the supernatant liquid resulting; washing with pure water, however, causes an opalescence which cannot be removed by filtration. The author shows that this is due to part of the zinc sulphide assuming a colloidal form in presence of pure water, whilst the addition of an ammonium salt to the solution renders the sulphide again insoluble.

The precipitate deposited on adding hydrogen sulphide to an ammoniacal zinc solution has the composition  $\text{ZnS}$ . After sweeping out as much hydrogen sulphide as possible from the opalescent colloidal solution by passing a current of an inert gas through it, rather less zinc (64.8 instead of 67.0) remains in the solution than would correspond with the sulphur present, if the latter existed merely as zinc sulphide. The same conclusion is arrived at on precipitating the colloidal sulphide by heating, determining the hydrogen sulphide evolved, and weighing the precipitated sulphide. The colloidal sulphide might have the composition  $5\text{ZnS} \cdot \text{H}_2\text{S}$ , although the hydrogen sulphide present is probably only mechanically retained by the cold solution. W. J. P.

**Thallium Triiodide.** By H. L. WELLS and S. L. PENFIELD (*Zeit. anorg. Chem.*, 6, 312—316).—By digesting thallium iodide and iodine with alcohol, and allowing the solution to evaporate over sulphuric acid, rhombic crystals of thallium triiodide,  $\text{TlI}_3$ , were obtained, isomorphous with those of the triiodides of rubidium and caesium (Abstr., 1892, 773, and 1893, ii, 67);  $a : b : c = 0.6828 : 1 : 1.1217$  for  $\text{TlI}_3$ ;  $= 0.6858 : 1 : 1.1234$  for  $\text{RbI}_3$ ;  $= 0.6824 : 1 : 1.1051$  for  $\text{CsI}_3$ . As the authors claim to have proved that the latter salts are molecular compounds, the same follows for thallium triiodide, in which compound thallium is then really univalent. As thallium exhibits so many analogies with the alkali metals, it was thought that it might possibly be a mixture of the two alkali metals, with atomic weights of about 170 and 220, that are missing in Mendeléeff's table. No separation could, however, be effected by fractional crystallisation of the nitrate. C. F. B.

**Action of Copper Sulphate and Sulphuric acid on Metallic Copper.** By A. SCHUSTER (*Proc. Roy. Soc.*, 55, 84—85).—The author gives details of some experiments performed a few years ago, but hitherto unpublished, which prove that when copper is placed in a copper sulphate solution containing free sulphuric acid, and the tubes exhausted of air, the diminution in the weight of the copper is quite insignificant compared to what takes place in the presence of air. A similar behaviour is noticed in sulphuric acid alone. H. C.

**Mercurous Sulphide.** By U. ANTONY and Q. SESTINI (*Gazzetta*, 24, i, 193—198).—Mercurous sulphide,  $\text{Hg}_2\text{S}$ , was described by Sef-

ström and by Brande, but their product was supposed by Guibourt and by Barfoed (*Jahresb.*, 1864, 282) to consist of a mixture of mercuric sulphide and mercury.

On passing a stream of hydrogen sulphide through potassium sulphate solution containing mercurous chloride or acetate in suspension, at  $-10^{\circ}$ , a black powder consisting of mercuric sulphide and mercury is deposited. A mixture of dry hydrogen sulphide and carbonic anhydride, however, acts on pure, dry mercurous chloride at  $-10^{\circ}$  with formation of mercurous sulphide; the carbonic anhydride is employed merely to dilute the hydrogen chloride evolved. Mercurous sulphide is also obtained by the action of dry hydrogen sulphide on dry mercurous acetate at  $-10^{\circ}$ , no gaseous diluent being necessary in this case; the salt is stable at  $-10^{\circ}$ , but decomposes into mercuric sulphide and mercury if the temperature rises above  $0^{\circ}$ . Mercurous sulphide may be distinguished from the mixture of mercuric sulphide and mercury by its behaviour towards a mixture of dry hydrogen chloride and carbonic anhydride. On passing these gases over the mixture containing the mercuric salt, no action occurs at either low or ordinary temperatures. At  $-18^{\circ}$  the gas has practically no action on mercurous sulphide; at  $-12^{\circ}$  the salt is slowly converted into mercurous chloride, whilst at  $0^{\circ}$  the conversion proceeds rapidly. Above  $0^{\circ}$  the action becomes more sluggish as the temperature rises, until at  $+18^{\circ}$  no mercurous chloride at all is produced; this is accounted for by the fact that the mercurous salt is completely decomposed into mercuric sulphide and mercury at this temperature.

Mercurous sulphide is a black powder which is not affected by the alkali hydroxides, ammonia, ammonium sulphide, or dilute nitric and hydrochloric acids below  $0^{\circ}$ ; fuming nitric acid, however, rapidly oxidises it. It readily dissolves in sodium or potassium sulphide below  $0^{\circ}$ , giving a limpid solution which, as the temperature rises, deposits mercury in a very fine state of subdivision. W. J. P.

**Allotropic Changes of Iron.** By G. CHARPY (*Compt. rend.*, 118, 868—870).—A number of bars of steel were subjected to tensile strain, and, at the same time, were heated at a definite temperature. It was found that although the breaking strain at first decidedly increases with the temperature and afterwards diminishes, the change which produces the rectilinear break (this vol., ii, 237) diminishes continuously, and the break disappears above a certain temperature. The curves representing the earlier stages are analogous to those representing changes of state at different temperatures.

The curves representing flexion and compression also show a rectilinear portion if the steel is annealed, but not if the steel has been tempered or subjected to cold-hammering.

The curve representing the effect of tensile strain is not materially affected by somewhat wide variations in the duration of the test.

C. H. B.

**Combination of Molybdenum Dioxide and Bisulphide with Alkali Cyanides.** By E. PÉCHARD (*Compt. rend.*, 118, 804—807).—

An acid solution of molybdenum dioxide can be obtained without the aid of metallic molybdenum, by adding potassium iodide to a solution of an alkali molybdate in excess of hydrochloric acid, and boiling for a long time, or by electrolysing a solution of ammonium molybdate in hydrochloric or oxalic acid. When the acid liquids are mixed with potassium hydroxide, hydrated molybdenum dioxide is precipitated. If a hot, strongly ammoniacal solution is electrolysed, a brown deposit forms very slowly on the negative electrode, and consists of hydrated molybdenum dioxide, and not of the hydrated sesquioxide as Smith has stated (*Ber.*, 1880, 753).

Molybdenum dioxide dissolves very easily in an aqueous solution of potassium cyanide, forming a strongly alkaline blue liquid, which after concentration deposits blue needles of the compound  $\text{MoO}_2\text{Cy}_2 \cdot 2\text{KCy}$ , which can be purified by digestion with alcohol, in which it is practically insoluble. This compound is very soluble in water, and its blue solution is stable in presence of alkalis. When treated with dilute acids, it becomes brown; with concentrated acids, it yields hydrocyanic acid and a brown precipitate of the compound  $\text{MoO}_2\text{Cy}_2$ , and if the latter is left in contact with acids, it yields hydrocyanic acid and a solution of the dioxide, the change being accelerated by heating. With solutions of metallic salts, the solution of the blue double cyanides yields heavy precipitates having characteristic colours; bluish-white with lead, pale brown with copper, greenish-blue with mercuric salts, and dark brown with silver salts. The silver compound has the composition  $\text{MoO}_2\text{Cy}_2 \cdot 2\text{AgCy}$ .

An acid solution of the dioxide when treated with hydrogen sulphide yields a reddish-brown precipitate of the bisulphide, and the latter dissolves readily in a warm solution of potassium cyanide forming a deep green liquid, which when concentrated yields slender, black needles of the compound  $\text{MoS}_2\text{Cy}_2 \cdot 2\text{KCy}$ . It can also be obtained by boiling a solution of potassium thiomolybdate with an excess of potassium cyanide, until the red colour of the liquid has completely changed to green. When treated with hot acids, it yields hydrocyanic acid and molybdenum bisulphide. The green solution of the salt is precipitated by alcohol; with metallic solutions, it gives precipitates with characteristic colours, *e.g.*, green with lead salts, red with silver salts, brown with copper salts.

It is molybdenum dioxide that gives the characteristic red coloration with thiocyanates, but the author was unable to isolate the red compound. A mixture of potassium thiocyanate and acid potassium molybdate, which becomes purple when mixed with a strong acid, becomes deep yellow only with acetic acid, and when the liquid is concentrated it yields yellow prisms of the compound



which is decomposed by water with separation of potassium trimolybdate. An analogous ammonium compound, stable in presence of acetic acid, but decomposed by water, can also be obtained. Both salts dissolve in dilute hydrochloric acid, forming an orange liquid, which gives the purple coloration characteristic of molybdenum dioxide when mixed with zinc and ether.

C. H. B.

## Mineralogical Chemistry.

**Nickeliferous Iron Pyrites from Sudbury, Ontario.** By T. L. WALKER (*Amer. J. Sci.*, [3], 47, 312—314).—The principal nickel ore of the Sudbury district is nickeliferous pyrrhotite, but at the Murray Mine nickeliferous iron pyrites also occurs. Marcasite, magnetite, galena, copper pyrites, and nickeliferous pyrrhotite are the associated minerals. At first only massive specimens were found, but in 1893 several bright cubic crystals were obtained. Specific gravity, colour, lustre, and magnetic properties are the same as in ordinary iron pyrites. Analysis of undecomposed massive pieces yielded

Ni.	Fe.	S.	H <sub>2</sub> O.	Cu.	Insoluble.	As.
4.34	39.70	49.31	0.10	trace	5.76	none

The mineral is thus iron pyrites, in which part of the iron is replaced by nickel, its composition being represented by the formula  $(\text{FeNi})\text{S}_2$ . B. H. B.

**Variscite from Utah.** By R. L. PACKARD (*Amer. J. Sci.*, [3], 47, 297—298).—A beautiful green mineral from a quartz vein near Lewiston, Utah, proved to have a composition the same as that of variscite, the analytical results being as follows.

H <sub>2</sub> O.	P <sub>2</sub> O <sub>5</sub> .	Al <sub>2</sub> O <sub>3</sub> .
22.95	44.40	32.65

The mineral is compact or crypto-crystalline and dull. Its sp. gr. is 2.62, and its hardness about 4. B. H. B.

**Analysis of a Molybdenum Mineral, and the Existence of a Ferrous Tetramolybdate.** By M. SPICA (*Gazzetta*, 24, i, 97—111).—The author has examined a crystalline quartzose rock from Stilo in Calabria; the several constituents of the rock were mechanically separated. It consisted of a siliceous gangue, biotite, and another mica, molybdenum bisulphide, iron pyrites with a little copper sulphide, anhydrous uranium molybdate,  $\text{U}_2(\text{MoO}_4)_3$ , ferrous tetramolybdate,  $\text{FeO}$ ,  $4\text{MoO}_3$ ,  $8\text{H}_2\text{O}$ , and another substance not yet completely examined.

The uranium trimolybdate occurs in yellow amorphous crusts, and has not previously been obtained either from natural or artificial sources. The ferrous tetramolybdate separated from a solution of the last above-mentioned constituent of the rock in hydrochloric acid; it is very sensitive to the action of light, and is deliquescent. It is very soluble in water, but less so in alcohol. W. J. P.

**Enstatite and the Products of its Alteration.** By K. JOHANSSON (*Zeit. Kryst. Min.*, 23, 152—155).—The author gives the results of an optical and chemical investigation of unaltered enstatite, and of the bastite-like products of its alteration. The specimens of enstatite analysed were obtained from Almekloväl, Söndmöre, and

from Ödegården, Bamle in Norway, and those of bastite-like material were from North America and from Kjørrestadkilen, Bamle.

B. H. B.

**Leucite in New Jersey.** By J. F. KEMP (*Amer. J. Sci.*, 47, 339—340).—The author recently described (Abstr., 1893, ii, 539) a basic dyke near Hamburg, New Jersey, which has been thought to contain leucite. A subsequent exploration at Rudeville, near Hamburg, has proved that there actually is in Sussex County, New Jersey, a leucite dyke rock, associated with the elæolite-syenite, and that the determination of a piece of the earlier described dyke by E. Hussak in 1882 as leucite-tephrite, although based on altered material, is substantiated by the discovery of satisfactorily fresh material.

B. H. B.

**Chemical Composition and Related Physical Properties of Topaz.** By S. L. PENFIELD and J. C. MINOR, jun. (*Amer. J. Sci.*, [3], 47, 387—396).—The chemical composition of topaz has never been satisfactorily settled. It occurred to the authors that perhaps the variations in the percentages of fluorine and the failure to yield a simple ratio are due to the partial replacement of fluorine by hydroxyl. Tests were accordingly made for water, and it has been found to be always present (compare Jannasch and Locke, this vol., ii, 284). The results of analyses of topaz from 10 localities show, as was anticipated, that fluorine has been replaced by hydroxyl, and the ratios indicate that  $\text{SiO}_2 : \text{Al}_2\text{O}_3 : \text{F} + \text{OH} = 1 : 1 : 2$ . In topaz, as in herderite, an increase in hydroxyl is accompanied by a decrease in specific gravity and an increase in the indices of refraction. In both minerals, the substitution of hydroxyl for fluorine causes a change in the lengths of the crystallographic axes.

B. H. B.

**Analysis of Nepheline.** By H. BERGHELL (*Zeit. Kryst. Min.*, 23, 157; from *Geol. Foren. Forhand.*, 13, 300).—At Iiwaara in Finland, in a rock known as ijolite, nepheline occurs in an unaltered condition. On analysis it gave the following results.

$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{CaO}$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	Total.
43.98	34.93	0.36	16.76	3.83	99.86

B. H. B.

**Milosin, Alexandrolite, and Avalite.** By S. M. LOSANITSCH (*Chem. News*, 69, 243—245).—Milosin and avalite are Servian minerals, the composition of which had hitherto not been established. A new green mineral occurring with milosin is termed alexandrolite by the author. Analysis of the three minerals gave the following results.

	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Cr}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{MgO}$	$\text{K}_2\text{O}$	$\text{H}_2\text{O}$	Total.
I.	76.37	30.18	9.75	0.91	trace	trace	13.76	100.88*
II.	52.07	20.76	13.74	2.22	trace	trace	10.88	99.67
III.	54.66	20.46	10.88	1.18	2.06	4.61	5.66	99.51

I. Milosin; II. Alexandrolite; III. Avalite.

B. H. B.

\* The figures given add up to 130.97. A formula suggested in the original for the mineral requires  $\text{SiO}_2$ , 45.35 per cent. only.

**Phonolitic Rocks from Black Hills.** By L. v. PIRSSON (*Amer. J. Sci.*, [3], 47, 341—346).—In the Black Hills of Dakota, there is an extremely interesting series of high-alkali rocks. A phonolite from this region, described by the author, gave, on analysis, the following results.

SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	BaO.	MgO.	Na <sub>2</sub> O.
61·08	0·18	18·71	1·91	0·63	trace	1·58	0·05	0·08	8·68
			K <sub>2</sub> O.	H <sub>2</sub> O.	Cl.	SO <sub>3</sub> .			
			4·63	2·21	0·12	trace.			

The sp. gr. is 2·582. The very small amount of bivalent metallic oxides present and the great excess of soda over potash are noteworthy.

B. H. B.

**Analysis of a Meteorite from Zabrodje.** By P. MELIKOFF and L. PISSARJEWSKY (*Ber.*, 27, 1235—1238).—This meteorite fell on September 22, 1893, at Zabrodje in the province of Wilna; it weighs 3155 grams, the sp. gr. = 3·71 at 20°. It contained considerable quantities of ferrous sulphide and nickel iron, NiFe<sub>8</sub> (Taënite), together with small crystals of ferrous chromate; 59·08 per cent. was soluble in hydrochloric acid. The silicates had the following composition.

SiO <sub>2</sub> .	MgO.	CaO.	FeO.	MnO.	Al <sub>2</sub> O <sub>3</sub> .	Na <sub>2</sub> O.	K <sub>2</sub> O.	Total.
39·39	22·37	2·32	13·84	1·11	2·12	1·21	0·41	82·77

The composition of the meteorite was

NiFe <sub>8</sub> .	FeS.	P <sub>2</sub> O <sub>5</sub> .	FeCrO <sub>4</sub> .	Olivine.	Insoluble silicate.	Total.
9·31	6·6	0·19	0·7	42·77	40	99·57

The insoluble silicates probably consist of albite (11·26 per cent.) and of bronzite (28·74 per cent.).

J. B. T.

**Mineral Water of Gyrenbad.** By F. P. TREADWELL (*Arch. Pharm.*, 231, 579—591).—The upper spring of Gyrenbad (Canton Zürich) yields 10—15 litres of water per minute. The water is clear, colourless, and odourless. The temperature of the water on the 26th of February, 1893, was 8°, the temperature of the air being 5·2°; the sp. gr. was 1·00043 at 12·9°. The results were as follows in parts per 10,000.

Cl.	SO <sub>3</sub> .	CO <sub>2</sub> .	N <sub>2</sub> O <sub>5</sub> .	AlPO <sub>4</sub> .	K <sub>2</sub> O.
0·005561	0·065098	3·614400	0·010310	0·000200	0·010563
Na <sub>2</sub> O.	(NH <sub>4</sub> ) <sub>2</sub> O.	CaO.	BaO.	MgO.	SiO <sub>2</sub> .
0·016237	0·003030	1·400600	trace	0·422190	0·060120
	FeO.	Organic matter.	Total residue.		
	0·000054	0·066369	3·558050		

CO<sub>2</sub> (free and half combined) 1180·2 c.c. at 8° and 770 mm.

CO<sub>2</sub> (free) 331·43 c.c. at 8° and 770 mm.



A centinormal solution of potassium permanganate immediately produced a pink coloration in 500 c.c. of the water acidified with sulphuric acid.

M. O. F.

## Physiological Chemistry.

**Assimilation of Inorganic Substances.** By J. NEUMANN (*Chem. Centr.*, 1894, i, 561—562; from *J. Landw.*, 41, 343—380).—A calf was fed on milk, then for a second period on milk *plus* 9 grams of calcium phosphate, then for a third period on milk *plus* 12 grams of calcium phosphate daily; the following results were obtained.

	1st period.	2nd period.	3rd period.
<b>a. Lime.</b>			
Taken in.....	24·63	27·88	29·19
Excreted.....	12·86	14·42	16·77
Assimilated .....	11·77	12·96	12·42
<b>b. <math>P_2O_5</math>.</b>			
Taken in.....	30·46	32·83	34·33
Excreted.....	14·91	16·87	18·39
Assimilated ..	15·55	15·96	15·94

That is, about 50 per cent. was assimilated in the first period, and the quantity absorbed varies but little, although the amount ingested was increased in the second and third periods, and so the percentage assimilated fell.

In another research, however, in which 7·5 grams of calcium carbonate was added to the milk, the quantity assimilated rose to 61 per cent.

W. D. H.

**Digestibility and Nutritive Value of Margarine.** By A. JOLLIS (*Monatsh.*, 15, 147—163).—From experiments on dogs, conducted in the usual way by comparing ingesta with egesta, the conclusion is drawn that margarine, so far as regards digestibility and nutritive value, is exactly similar to true butter.

W. D. H.

**Proteid Metabolism.** By A. RITTER (*Chem. Centr.*, 1894, i, 592; from *Sitz. Ges. Morph. u. Physiol. Munchen*, 9, ii, 62).—Some recent observers have stated that human beings can maintain nitrogenous equilibrium on considerably less proteid than was formerly stated to be necessary. The present research on two men, carried out in the usual way, does not confirm this. Both lost considerably both in weight and health; the sparing action of fat and carbohydrate on proteid metabolism is therefore limited.

W. D. H.

**The Varieties of Sugar formed by Animal Ferments from Starch and Glycogen.** By E. KÜLZ and J. VOGEL (*Zeit. Biol.*, 108—124).—The starch used was rice starch in a 5 per cent. solution. It was subjected to the action of the ferment, and the sugar formed identified by the use of the phenylhydrazine reaction; the osazone being subjected to elementary analysis.

As the result of the action of human parotid saliva, the sugar formed yielded isomaltosazone.

Mixed human saliva produced isomaltose at first, later, maltose was formed in addition, and even small quantities of dextrose.

Dogs' saliva gave rise to isomaltose.

Ox pancreas acted similarly.

The remaining experiments relate to glycogen. Human parotid saliva produced isomaltose and maltose in the proportion 1 : 2 from liver glycogen. From muscle glycogen, small quantities of the same saliva produced isomaltose, with small quantities of maltose and dextrose. Large quantities of the same saliva produced maltose only.

Ox pancreas and liver glycogen led to the formation of isomaltose with a very small admixture of maltose. Ox pancreas and muscle glycogen led to the formation of isomaltose with a very small admixture of dextrose. Diastase produced the same products from muscle glycogen.

W. D. H.

**Chemical Changes in Cartilage during Ossification.** By C. CHABRIÉ (*Compt. rend.*, 118, 1057—1060).—The process of ossification is usually regarded as a process in which the cartilaginous (chondrogenous) basis is replaced by osseous (gelatin-yielding) tissue. The present paper gives certain theoretical chemical reasons for believing that the change is not such a replacement, but an actual conversion of chondrogen into collagen.

W. D. H.

**Protagon.** By W. G. RUPPEL (*Zeit. Biol.*, 31, 86—100).—Protagon was separated in a crystalline form from the brains of human beings and oxen. Elementary analysis gives numbers agreeing closely with those of previous observers, and thus the view of Gamgee and Blankenhorn, which is supported by Baumstark, that protagon is a chemical unit, is confirmed.

The following table gives the principal analyses hitherto made.

	Liebreich.	Gamgee and Blankenhorn.	Baumstark.	Kossel.	Ruppel.	
					Ox.	Human.
C....	66.74	66.39	66.48	66.25	66.29	66.51
H....	11.74	10.69	11.12	11.13	10.75	10.88
N....	2.80	2.39	2.35	3.25	2.32	2.55
P....	1.23	1.068	1.02	0.97	1.13	1.188
S....	—	—	—	0.51	0.096	—

W. D. H.

**Fats of Human Milk.** By W. G. RUPPEL (*Zeit. Biol.*, 31, 1—11).—The fatty acids found in human milk are butyric, caproic, capric, myristic, palmitic, stearic, and oleic acids all combined with glycerol. The presence of formic acid is also inferred from its reducing action, but not by any further tests. Quantitative analysis is not given, human milk is, however, poor in the volatile acids.

W. D. H.

**Crystalline Acids of Human Bile.** By LASSAR-COHN (*Ber.*, 27, 1339—1346).—The method previously employed by the author for the investigation of ox bile (Abstr., 1892, 1114; 1893, ii, 220) has now been applied to that of human bile. The bile was hydrolysed by boiling it for 24 hours with 6 per cent. potassium hydroxide, this concentration being maintained by the addition of water from time to time. The results may be summed up as follows:—There is obtained from human bile one more acid than from ox bile, namely, *fellenic* acid,  $C_{23}H_{38}O_4$ . This is a tasteless compound melting at 166—169°; it is homologous with choleic acid, and apparently distinct from Schotten's fellenic acid (Abstr., 1887, 606). The other substances separated were cholic acid,  $C_{24}H_{40}O_6$ , choleic acid,  $C_{24}H_{40}O_4$ , besides fatty acids and uncrystallisable resin.

A. R. L.

**Urea Formation.** By A. GAUTIER (*Compt. rend.*, 118, 902—904), by A. CHAUVEAU (*ibid.*, 904—906), by BERTHELOT (*ibid.*, 906—907), and by KAUFMANN (*ibid.*, 937—939).—It is admitted that urea is in great part formed in the liver from proteid material. Chauveau regards this as due to oxidation, whilst Gautier considers that in the liver and other organs, urea is the product of fermentation (hydrolysis), and that oxygen is unnecessary. This he supports by stating that—(1) protoplasm is usually reducing in its action, and in the liver glycogen, sugar and fat are formed, by reduction, simultaneously with the urea; (2) Ehrlich's experiments with sodium sulphindigotate and other pigments show that the reducing action of living tissues during life is especially marked in the liver; (3) Richet's experiments show that urea is formed in a piece of liver plunged into melted paraffin where there can be no access of oxygen. In the two papers that follow the first, it is pointed out that the liver normally is being traversed by blood rich in oxygen, and that the formation of urea is on all fours with that of carbonic anhydride.

Kaufmann's paper relates to the site of urea formation, and the conclusions he draws from his experiments are—(1) that the formation of urea is not entirely localised in the liver; all other tissues produce a certain quantity; (2) nevertheless the liver is the seat of most active and abundant production of urea; (3) that this urea formation is produced by the interaction of the blood and by metabolic phenomena in the tissues.

W. D. H.

**Chemical Composition of a Fatty Tumour.** By W. G. RUPPEL (*Zeit. Biol.*, 31, 101—107).—The results of the analysis may be briefly stated as follows.

	Grams.	
Connective tissue .....	11.0 =	1.90 per cent.
Fat .....	452.0 =	78.07    "
Water .....	116.0 =	20.03    "

Total weight ..... 579.0

The 452 grams of fat contained:—

	Grams.	
Free fatty acids.....	4.52 =	1.0 per cent.
Oleic acid.....	293.80 =	65.0    "
Fixed acids (mostly stearic)	166.22 =	23.5    "
Glycerol, volatile acids (especially capric and butyric), and unsaponifiable substance.....	47.46 =	10.5    "

W. D. H.

**Poisoning by Pyrogallol and its Detection.** By D. VITALI (*L'Orosi*, 17, 37—45).—Death resulted from the administration of 0.20 gram of pyrogallol, in several doses, to a dog weighing 8 kilos. The phenol can be detected in the urine after the first dose, but not after subsequent doses, its oxidation products only being then found.

W. J. P.

## Chemistry of Vegetable Physiology and Agriculture.

**Chemical Constituents of *Ilex Paraguayensis*.** By H. KUNZ-KRAUSE (*Arch. Pharm.*, 231, 613—640).—The chemistry of the maté leaf has not been the subject of much investigation within recent years. The author refers to caffeine and tannic acid, together with proteids and inorganic salts, as having already been shown by various chemists to occur in the leaf of the Brazilian holly, and then describes results which prove the presence of combined choline, an optically inactive sugar arising from the hydrolysis of the tannin present, and soluble potassium and magnesium salts, amounting to more than 1 per cent. of the dried leaf. Brazilian holly does not contain ilixanthin.

The author has submitted the tannin derived from maté to a close comparison with that obtained from coffee, and is able to confirm Rochleder's conclusion that these two acids are identical. This is shown by numerous reactions common to both, and also by the fact that hydrolysis, with concentrated potash, gives rise to the dihydroxycinnamic acid already obtained by Hlasiwetz from caffe-tannic acid (*Annalen*, 142, 221 and 357).

Dihydroxycinnamic acid,  $C_9H_7O_4$ ,  $[COOH : (OH)_2 = 1 : 3 : 4]$ , separates from alcohol in pale-brown aggregates, single crystals from an aqueous solution being light yellow. With bivalent metals it forms three series of salts—normal, monobasic, and bibasic. Fusion

takes place at 197—201°, accompanied by evolution of carbonic anhydride; the residue most probably contains the hitherto unknown 3:4-dihydroxycinnamene, which shows the colour reaction with strong sulphuric acid characteristic of its methyl ether (Abstr., 1881, 740), and also yields catechol when submitted to dry distillation.

The tannin from maté is not readily attacked by hydrochloric acid, but bromine water is decolorised by its aqueous solution with the formation of bromodihydroxycinnamic acid, although the direct action of bromine on dihydroxycinnamic acid gives rise to a dibromo-derivative.

Another proof of the identity of the tannins derived from coffee and from maté is the decomposition of the latter by Liebermann's reagent, with the formation of glucose, catechol, oxalic acid, and hydrogen cyanide, the intermediate product being dihydroxycinnamic acid. The glucose from this source is an optically inactive syrup, which yields a crystalline osazone, and reduces Fehling's solution. Hence the occurrence of glucose in the aqueous extract of the dried leaf is explained by the decomposition of a portion of the tannin present.

M. O. F.

**Balsam of Tamacoaré; a Brazilian Vegetable Oil.** By F. PFAFF (*Arch. Pharm.*, 231, 522—541).—Tamacoaré balsam is viscid, and of a yellowish-brown colour; it is heavier than water, with which it forms an emulsion, but is soluble in all other ordinary solvents. When distilled, either under atmospheric pressure or in a vacuum, it undergoes decomposition, and, although a clear oil passes over in a current of superheated steam, the distillate soon becomes brown as the temperature rises.

A study of the chemical properties of Tamacoaré balsam shows it to consist of an individual substance of the formula  $C_{23}H_{34}O_6$ . By mixing alcoholic solutions of the oil and mercuric chloride, a derivative of the composition  $C_{23}H_{32}O_6, HgCl$  is obtained, crystallising in tufts of colourless needles, soluble in cold chloroform and ether, but insoluble in boiling alcohol. On passing hydrogen sulphide through a solution of the compound in ether and alcohol, to which a few drops of hydrochloric acid have been added, mercuric sulphide is precipitated, whilst the filtrate contains the original oil. One specimen of Tamacoaré balsam, after remaining in a stoppered flask for two years, deposited colourless crystals identical in chemical properties with the oil, which is regenerated by dissolving the crystalline product in any ordinary solvent (alcohol excepted), and evaporating. \*Decomposition of the oil with concentrated alkalis gives rise to numerous products, of which, however, normal butyric and caprylic acids only have been identified.

M. O. F.

**Blay-Hitam; a Malayan Arrow Poison.** By H. SANTESSON and C. G. SANTESSON (*Arch. Pharm.*, 231, 591—612).—The authors have submitted the bark of the Blay-Hitam plant to a careful examination, and have succeeded in isolating, as its chief chemical constituent, an alkaloid which corresponds completely in chemical and toxic properties with brucine. The same alkaloid is present in

the wood and sap, the latter also giving uncertain indications of the presence of strychnine.

M. O. F.

**Composition of the Ash of Olive Mark Extracted with Water and with Carbon Bisulphide.** By D. MARTELLI (*Staz. Sper. Agrar.*, 25, 60—72).—The pasty substance obtained after the expression of the oil from olives is sometimes employed as cattle food or manure, or it is further extracted with water or with carbon bisulphide. The residue may be used as food or manure, and is frequently used as fuel for heating the kettles in the oil factories. Samples of ashes from various sources were obtained and analysed. There is a good deal of difference in the results, owing to the difference in the soils on which the olives were grown, and also to differences in the manner in which the olives were treated. The most valuable ashes, as manures, were those obtained from residues extracted with carbon bisulphide; the pure ashes contained  $K_2O$ , 19 to 32 per cent.;  $CaO$ , 16—33 per cent.;  $P_2O_5$ , 3 to over 5 per cent.;  $MgO$ , 3 to 3·7 per cent.; and  $SO_3$ , 1 to 10·7 per cent. The residues extracted with water gave less nutritive ashes, especially as regards potash (4·6—20 per cent.); phosphoric anhydride was also lower (3·7—4·3 per cent.). Chlorine, which was present in the ash from the carbon bisulphide residue to the amount of 0·5—4 per cent., was found only in traces in the ash of residues washed with water. The author points out the importance of utilising the ashes for manuring, either alone or mixed with nitrogenous matter, and sufficient acid to neutralise the alkali.

N. H. M.

## Analytical Chemistry.

**Laboratory Apparatus** By F. ANDERLINI (*Gazzetta*, 24, i, 150—156).—In place of the ordinary Geissler potash bulbs used in organic analysis, the author recommends a modification in which three bulbs are arranged one above the other inside a fourth; the whole apparatus stands on a foot, and can be improved by the addition of a tap closing both entrance and exit tubes.

An improved form of calcium chloride drying tube for use in organic analysis is also described; it consists of a cylinder standing on a foot, and containing an internal tube down which the products of combustion pass. The whole apparatus is filled with calcium chloride, and both inlet and outlet are closed by a tap at the top of the apparatus. Towers, of somewhat similar construction to the preceding, may be advantageously employed in drying the air or oxygen used in the analysis.

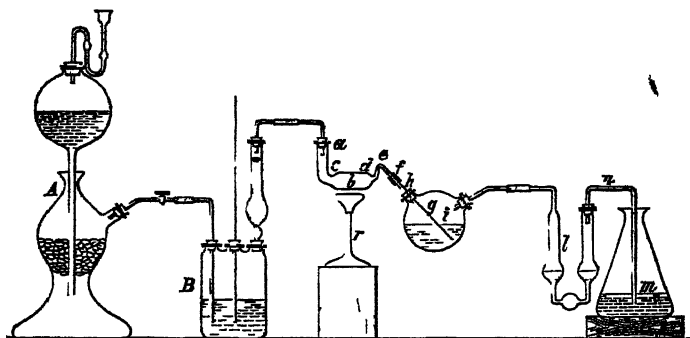
The author also describes improved forms of fractionating columns and a safety separating funnel.

W. J. P.

**Estimation of Moisture in Wood Pulps.** By J. C. BELL (*J. Soc. Chem. Ind.*, 1894, 117—118).—The author recommends that the sample should be dried to constant weight at 100°, and then a definite percentage of moisture allowed. The exact amount to be allowed should be fixed by a joint committee of manufacturers and analysts.

L. DE K.

**Estimation of Sulphur in Sulphides, and Simultaneous Estimation of the Arsenic present.** By P. JANNASCH (*Zeit. anorg. Chem.*, 6, 303—309).—The apparatus used is figured below. A is an apparatus for generating hydrogen chloride; B contains sulphuric acid, and has a calcium chloride tube attached; the vessel *a*, *c*, *b*, *d*, *e*, *f* is of hard glass; *h* is a ground-glass joint; *i* contains 3 per cent. aqueous hydrogen peroxide, with some strong nitric acid added; *l* and *m* the same mixture, diluted with an equal volume of water. About 0.6 gram of the finely-powdered mineral is placed in the vessel *a*, *f*, and first heated with a flat flame Bunsen burner for about half an hour in a current of dry oxygen; the sulphur and most of the arsenic are oxidised and carried over. The oxygen apparatus is then disconnected, and replaced by A, B; and *a*, *f* is immersed in boiling water, while a rapid current of hydrogen chloride is passed through for 1½—2 hours. The contents of *i*, *l*, and *m* are now mixed, and concentrated to 20—25 c.c., small quantities of strong nitric acid being added from time to time. The residue is diluted to 200 c.c., the sulphuric acid precipitated with a very slight excess of barium chloride, and the barium sulphate collected and weighed. The excess of barium in the filtrate is precipitated with a very slight excess of sulphuric acid, the filtered solution is evaporated to a small bulk, and made alkaline with ammonia, and the arsenic is then precipitated with a slight excess of magnesium chloride, the precipitate being treated as described in Abstr., 1892, 658.



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C. F. B.

**Estimation of Arsenic in Copper.** By F. PLATTEN (*J. Soc. Chem. Ind.*, 1894, 324—326).—The author, having satisfied himself that arsenious sulphide is completely decomposed by boiling with a

large amount of water, recommends the following process for the estimation of arsenic in copper.

The metal is heated, as usual, with ferric oxide and hydrochloric acid. The distillate is precipitated with hydrogen sulphide, and the impure arsenious sulphide is collected. Instead of directly weighing it, it is boiled for some time with about half a litre of water, and, after cooling, the arsenic is titrated with centinormal iodine solution in the usual manner.

L. DE K.

**Detection of Arsenic when associated with Antimony and Tin.** By F. A. GOOCH and B. HODGE (*Amer. J. Sci.*, [3], 47, 382—385).—The mixture containing the three metals is distilled with 3 grams of potassium iodide dissolved in 5 c.c. of water and an equal volume of strong hydrochloric acid. The distillate is condensed in 10 c.c. of dilute hydrochloric acid (1 : 1). The free iodine is removed by the cautious addition of stannous chloride, and the arsenic is then precipitated by hydrogen sulphide. Traces of antimony, which may have passed over, and the added tin, are not precipitated in presence of such a large excess of acid. If it be desired to completely remove the arsenic, the residue in the flask must be distilled a few times more with hydrochloric acid. The remaining liquid is afterwards tested for tin and antimony in the usual manner.

The apparatus employed is essentially the one devised by Mohr, and consists of a 25 c.c. flask, fitted by means of a rubber stopper to a pipette, bent, drawn out at the lower end and dipped into a test tube, which is at the same time supported and cooled in a flask partly filled with water. The pipette tube should be wide enough to prevent the formation of bubbles within it, and the bulb large enough to retain any liquid which may happen to force itself back by accidental cooling of the flask.

L. DE K.

**Testing for Boric acid in Wine-ash.** By P. KULISCH (*Zeit. angew. Chem.*, 1894, 147—148).—Ripper, who first detected the presence of boric acid in the ash of wine, recommends that the mineral matter of 25—50 c.c. of wine should be dissolved in 10 c.c. of water and 2 c.c. of hydrochloric acid (sp. gr. 1.19). By means of faintly coloured turmeric paper, the boric acid reaction may then be readily obtained.

The author, however, recommends simply dissolving the ash in a few drops of acid, and testing with paper of a decided yellow colour. The test is then much more satisfactory.

L. DE K.

**Estimation of Carbonic Anhydride in Presence of Soluble Sulphides.** By A. WOLKOWICZ (*Zeit. angew. Chem.*, 1894, 165).—The author uses the apparatus recommended by Fresenius, but, before liberating the carbonic acid by means of hydrochloric acid, the substance is covered with a 20 per cent. solution of copper chloride. Copper sulphate must not be used, as this might form a cake of an insoluble sulphate and so prevent the proper action of the acid.

The hydrogen sulphide is completely retained by the copper solution, and the carbonic acid is dried and finally absorbed in weighed soda-lime tubes.

L. DE K.



**New Method for the Volumetric Estimation of Magnesium.**

By G. VENTUROLI (*Gazzetta*, 24, i, 213—218).—On treating a solution of a magnesium salt with disodium hydrogen phosphate, magnesium hydrogen phosphate is formed; this is converted, by boiling, into a mixture of trimagnesium diphosphate and magnesium tetrahydrogen diphosphate,  $4\text{MgHPO}_4 = \text{Mg}_3(\text{PO}_4)_2 + \text{MgH}_4(\text{PO}_4)_2$ . Since the latter salt has an acid reaction, its quantity can be determined by titration with standard alkali solution.

A concentrated aqueous solution, containing about 45 parts of disodium hydrogen phosphate for every part of magnesia to be estimated, is boiled, a little phenolphthaleïn being added; during the boiling, the neutral magnesium solution is run in until the red tint vanishes. The solution is then titrated with decinormal soda solution until the red colour reappears, care being taken not to add soda solution after the appearance of the pink tint. The quantity of magnesium in the solution added to the phosphate can then be calculated, knowing that 2 mols. of magnesia,  $\text{MgO}$ , are equivalent to 1 mol. of soda,  $\text{NaHO}$ .

The process may also be employed for the estimation of calcium; the titration may be performed in the cold; the reaction which occurs is somewhat different:  $5\text{Na}_2\text{HPO}_4 + 4\text{CaCl}_2 = 8\text{NaCl} + \text{Ca}_4\text{H}(\text{PO}_4)_3 + 2\text{NaH}_2\text{PO}_4$ . The tetracalcium hydrogen triphosphate separates from the solution, and does not affect the analytical results; 2 mols. of lime,  $\text{CaO}$ , are equivalent to one of soda,  $\text{NaHO}$ .

Test analyses show that these methods possess considerable accuracy. A similar process is probably also applicable for the estimation of barium and strontium.

W. J. P.

**Estimation of Calcium and Magnesium.** By O. FORTE (*Gazzetta*, 24, i, 207—213).—Calcium and magnesium may be estimated, when in a solution containing no other metals, by precipitating as carbonates, igniting, and weighing the mixed oxides; the product is then converted into sulphates, ignited, and again weighed.

W. J. P.

**Valuation of Zinc Dust.** By F. MEYER (*Zeit. angew. Chem.*, 1894, 231—232).—The author dissolves the sample in sulphuric acid and measures the volume of the hydrogen evolved. The apparatus consists of a generating flask, a reservoir containing dilute sulphuric acid (1 : 3), a graduated tube ending in a bulb with a stop-cock, and a connecting piece properly ground at each end and provided with a three-way stop-cock.

1 gram of the zinc dust is put into the generating flask, which is then fixed to the connecting piece and filled with water. After closing the stop-cock, the other end is fixed to the graduated tube, and the protruding end of the stop-cock is connected with the reservoir by means of an india-rubber tube. The stop-cock on the bulb is now opened, and the reservoir lifted up to fill the burette with acid, after which the cock is again closed. By opening the three-way stop-cock in the proper direction, the acid descends, in consequence of its greater specific gravity, into the generating flask, and liberates hydro-

gen, which collects in the graduated tube, the liquid being driven back into the reservoir.

When the action is over, the liquids in the reservoir and burette are levelled, and the volume of the hydrogen is read off and corrected for temperature and pressure. The percentage of zinc in the sample is then found by a simple calculation. L. DE K.

**Estimation of Cadmium.** By M. MUSPRATT (*J. Soc. Chem. Ind.*, 1894, 211—213).—Cadmium may be accurately estimated as oxide, the ignition being effected in a stream of oxygen, but the oxide does not stand the heat of a gas blowpipe, suffering serious diminution in weight. The estimation as sulphide is also very good, but the precipitate is often difficult to filter and wash.

The preference, however, should be given to the electrolytic methods on account of their simplicity, cleanliness, and accuracy; the chief precautions to be taken being the use of dilute solutions and weak currents. The metal is best deposited from a weak sulphuric acid solution, and it has little tendency to oxidise. L. DE K.

**Estimation of Manganese in Minerals and Metals.** By E. H. SANTEE (*J. Soc. Chem. Ind.*, 1894, 112—116).—The author criticises the various gravimetric and volumetric processes. The weighing of manganese as  $Mn_2O_4$  is utterly untrustworthy if the metal has been precipitated as hydrated dioxide; somewhat better results are obtained when the precipitated sulphide is ignited in contact with air. The weighing as pyrophosphate is accurate if the solution has been completely freed from other metals, which is, however, a very tedious operation. Pattinson's volumetric process (titration of the dioxide with ferrous sulphate), and Volhard's method (titration with potassium permanganate), are trustworthy when the standard solutions are checked with manganese oxide of exactly known composition. L. DE K.

**Estimation of Silicon and Aluminium in Iron.** By L. L. DE KONINCK (*Chem. Centr.*, 1894, i, 523; from *Rev. univ. Mines*, 14, 133).—The metal is first treated with nitric acid or nitro-hydrochloric acid, and precipitated with ammonia or ammonium hydrogen carbonate; if manganese is present, the iron must be precipitated with ammonium acetate. The ammonia should be free from silica; if not, it should be distilled, and the vapour condensed in the iron solution. The precipitate, after being collected on a filter, washed, and ignited, is placed in a weighed platinum boat and heated in a current of hydrogen chloride; the iron is then volatilised as chloride, whilst silica and alumina remain behind. To estimate the aluminium, the mixture is evaporated with hydrofluoric acid, or ignited with ammonium fluoride, which causes the silica to volatilise. The aluminium may contain other substances such as titanium and chromium, and must, therefore, be further tested. L. DE K.

**Acidimetric Estimation of Substances that form Molecular Compounds with Pleric acid.** By F. W. KÜSTER (*Ber.*, 27, VOL. LXVI. ii. 26)

1101—1105).—A strong flask is used, with an indiarubber stopper, through which passes a piece of glass tubing closed at the lower end, and with a small hole in the side rather above this end. It is thus possible to exhaust the flask, and then, by drawing up this tube until the hole is covered by the cork, to preserve a vacuum in the flask after the connection with the pump is broken. The substance to be examined is placed in the flask with a moderate excess of picric acid solution; this is a solution saturated at the ordinary temperature and of about N/20 strength. The flask, which should be filled about up to the neck, is then exhausted, and the whole heated on the water bath until all the substance has disappeared. It is then left for several hours, when the cold solution is filtered, and the excess of picric acid determined in the filtrate by titration with N/10 baryta water, phenolphthalein being used as an indicator. Good results were obtained with naphthalene, acenaphthene, and  $\alpha$ - and  $\beta$ -naphthol; in the last case a correction had to be made for the picrate remaining in solution (100 c.c. of the picric acid solution dissolves 0.0075 gram  $\beta$ -naphthol). With phenanthrene, quantitative results could not be obtained.

C. F. B.

**Volumetric Sugar Estimations.** By SAMELSON (*Zeit., angew. Chem.*, 1894, 267—268).—The gravimetric estimation of sugar by means of Fehling's solution has lately been again recommended instead of the volumetric process on account of its supposed greater accuracy.

The author thinks, however, that the volumetric process may be advantageously employed instead, if only the precaution be taken to ascertain the real titre of the alkaline copper solution, and not to blindly trust to its supposed strength.

L. DE K.

**Estimation of Acidity in Gastric Juice.** By J. J. KASAHN (*Chem. Centr.*, 1894, i, 481; from *Pharm. Zeit. Russ.*, 33, 21—22).—On adding hydrochloric acid to potassium hydrogen tartrate, the total acidity of the liquid is increased, owing to the liberation of the soluble tartaric acid. If the acidity of the mixture before the addition of the tartrate is called  $a$ , and that after,  $b$ , then  $3(b - a) =$  free hydrochloric acid. Organic acids and proteids do not interfere with the reaction. It may be applied to the estimation of hydrochloric acid in gastric contents, thus: 10 c.c. of the juice is titrated with sodium hydroxide ( $a$ ); 12 c.c. is mixed with 6 c.c. of 95 per cent. alcohol, and excess of tartrate added, the mixture being allowed to remain an hour, and then filtered. 15 c.c. ( $=$  10 c.c. of gastric juice) is then titrated as before ( $b$ ). A third titration in a control specimen is necessary, as potassium hydrogen tartrate is not insoluble in alcohol ( $c$ ). The quantity of free hydrochloric acid  $= [(b - c) - a] \times 3$ .

The results obtained come near to Günzburg's; after Ewald's test breakfast, the percentage of hydrochloric acid in the human stomach is 0.02 to 0.04. The results came out lower than Sjöquist's, by whose method the acid united to proteids is also estimated.

W. D. H.

**Estimation of Essential Oils, especially in Oil of Cloves and Oil of Mace.** By W. LENZ (*Zeit. anal. Chem.*, 33, 193—200).—The following is suggested as an improvement on older processes for estimating the amount of oil obtainable from the spice:—10 to 20 grams of the powder is mixed with water in a 200 c.c. retort, the beak of which is inclined upwards, but at its middle is bent downwards at a right angle and connected with a condenser. 10 c.c. of olive oil is added to prevent frothing, and steam is passed through the mixture as long as any oil distils. The distillate, amounting to about 500 c.c., is saturated with sodium chloride and extracted by shaking with ether (50 c.c., three times). The ethereal solution is dried by digesting with 20 grams of fused calcium chloride for at least three days, and is then evaporated below 30° in a tared flask, through which a current of dry air is passed, until, at intervals of five minutes, its weight becomes constant. The percentage of eugenol in the oil is then determined by Thoms' method (*Abstr.*, 1892, 250). The high solubility of oil of cloves in a 50 per cent. aqueous solution of sodium salicylate led to experiments in which this solution was substituted for water in the retort. The average yield of oil from the water distillations was 17.75 per cent., containing 79.44 per cent. of eugenol, from the salicylate 19.45 per cent., containing 84.52 per cent. of eugenol, the latter yield agreeing better than the former with that obtained on the large scale. Similar experiments with mace, the oil of which is nearly insoluble in salicylate solution, gave one-fourth more oil with the salicylate than with water, and that the action is not due to a mere rise in the boiling point of the solution is shown by the fact that solutions of potassium acetate and of calcium chloride have no such effect. The behaviour of the salicylate seems rather to be due to its peculiar solvent action on the plant tissues, which renders it such a valuable liquid for mounting microscopic preparations.  
M. J. S.

**Detection of Adulteration in Lard.** By SAMELSON (*Zeit. anal. Chem.*, 33, 189—192).—A qualitative method for the detection of vegetable fats has long been a desideratum, and several such have been proposed, but neither Becchi's, Gantter's (*Abstr.*, 1893, ii, 440), nor Welmans' can be depended on in all cases, the two former sometimes failing to give any indication in cases of undoubted falsification, whilst the latter may give as distinct a coloration where the purity of the sample is unquestionable, as in cases of adulteration. The iodine absorption remains at present the only trustworthy test.

M. J. S.

**Detection of Cotton-seed Oil in Lard.** By E. J. BEVAN (*Analyst*, 19, 88—89).—The author examined a sample of genuine lard which, however, gave a decided silver reaction. By scraping off the top portion and taking a part of what lay underneath, to which the air had not penetrated, no silver reaction was obtained. The same result was obtained with bladder lard, and here the possibility of any mechanically deposited dirt being present was out of the question. Lard was then exposed in a still room in flat dishes, and after a week's exposure, it gave the reaction quite strongly. The

author can come to no other conclusion than that the effect observed is due to an oxidation process. After passing air for a few days through melted lard, a product was obtained which gave an intense reaction with silver solution. The substance formed is no doubt present in very minute amount, but there is quite enough to mislead, and give the impression that cotton-oil is really present.

L. DE K.

**Estimation of Moisture and Oil in Linseed Cake, &c.** By A. P. AITKEN (*J. Amer. Chem. Soc.*, 16, 114—122).—In estimating moisture by drying the sample in a water oven, it is generally found several per cent. too low, and this, of course, spoils the estimation of the oil; the common practice being to determine the moisture in one part of the sample and the joint moisture and oil in another portion.

The author has now greatly improved the process by drying the sample, contained in an aluminium boat, at 100° in a current of dry coal gas, previously brought to the same temperature. By this means, oxidation of the oil is prevented. The oil is estimated by introducing the dried sample into an extraction tube, which is closed at the beginning of the elongated end with a double wad of filter paper, and after any powder adhering to the sides has been brushed down, another wad is patted in on the top. The tube is now inserted in one of the holes of a zinc box, which is filled with warm water. The narrow end of the tube dips into a weighed flask, in case it be desired to check the result by a direct weighing of the oil. Ether is now poured into the tube and the tube is corked; when the ether begins to boil it rapidly runs into the flask. The extraction is repeated 15 to 20 times. The contents of the tube are now pushed by means of a thin glass ramrod into a weighed aluminium capsule; the wads are cleaned with a camel-hair brush, and after drying the exhausted powder for a short time at 100°, it is reweighed.

L. DE K.

**Estimation of Glycocine.** By C. S. FISCHER (*Zeit. physiol. Chem.*, 19, 164—178).—It is recommended that albuminoids, like gelatin; keratin, &c., may be estimated by the amount of amido-acids (glycocine, leucine, glutamic acid, &c.) formed from them. The present paper relates, however, to gelatin and the glycocine formed from it.

The glycocine is estimated by converting it, by the use of hydrochloric acid and benzoic chloride, into hippuric acid, which is crystallised out and weighed. Leucine, &c., may be estimated by forming similar benzoyl compounds.

W. D. H.

**Detection of Horse-Flesh.** By BRÄUTIGAM and EDELMANN (*Chem. Centr.*, 1894, i, 485; from *Pharm. Centr.-H.*, 35, 60—68).—This method of detecting horse-flesh depends on the fact that this form of meat contains 0.373 to 1.072 per cent. of glycogen, whilst that of other animals used as food contains none, or the merest trace. Ox flesh comes next to horse-flesh (0.204 per cent.). From this, the authors claim to be able to detect 5 to 10 per cent. of horse-flesh mixed with other meat. The same holds for horse liver used in sausages.

W. D. H.

## General and Physical Chemistry.

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**Spectrum of Oxygen at High Temperatures.** By J. JANSSEN (*Compt. rend.*, 118, 1007—1009).—When oxygen under various pressures is enclosed in a steel tube 10 m. long, provided with glass ends, and heated by means of a row of gas burners, the bands and lines of the spectrum show no appreciable variation between the ordinary temperature and 300°, but the gaseous column becomes distinctly more transparent to the spectrum as a whole.

When the oxygen is heated by means of a spiral of platinum wire enclosed in the tube and made incandescent by an electric current, no variations in the spectrum are observed in a tube 2.1 m. long with pressures reaching 100 atmos. and temperatures as high as 800—900°.

C. H. B.

**Symbol for denoting the Optical Activity of Compounds.** By H. LANDOLT (*Ber.*, 27, 1362—1364).—Ladenburg has recently stated (this vol., i, 307) that the rotatory power of *d*-coniine is  $[\alpha]_D = 15.6$ , and he draws attention to the fact that Landolt (*Das optische Drehungsvermögen*, 1879, 225) gives the value 17.9 on the authority of Schiff. Landolt, in reply, states that he, having observed that the natural base had a rotatory power of 15.6° in a 1 decimetre tube, concluded that Schiff's value was merely the observed angle, and accordingly divided this number by the sp. gr., using the value observed by Schiff, namely, 0.873 at 15°; he thus obtained 17.9 as the specific rotatory power. Schiff is unable to say definitely, but he believes that the value given by him (15.6°) had already been divided by the sp. gr. It is, however, to be observed that Schiff's value for the sp. gr. of the base, as to the accuracy of which he is certain, differs from that of Ladenburg (*loc. cit.*).

It is suggested that, to prevent confusion, authors shall employ the words "observed angle" and "specific rotatory power," the latter being taken in Biot's sense and denoted by the symbol  $[\alpha]$ , a small letter being affixed to indicate the particular light employed.

A. R. L.

**Specific Rotation of Dissolved Substances.** By A. AIGNAN (*Ann. Chim. Phys.*, [7], 1, 433—463).—If an optically active substance A having the rotatory power  $[\alpha]$  is dissolved in presence of an inactive substance B and a compound of A and B having the rotatory power  $[\alpha]$  is formed in the solution, it is evident, as Biot showed, that the rotatory power of the solution should show a point of discontinuity when the concentration attains a certain magnitude. For, suppose the solution to contain P of A and Q of B, and the ratio between the weights of A and B in the compound which they form to be  $n$ ; further let  $\omega$  be the rotation of a column of solution of thickness  $l$  and density  $\delta$ , and let the weight M of the solution be constant, then when  $Q < nP$

$$[\alpha] + \frac{[\alpha](n+1) - [\alpha]}{n} \cdot \frac{Q}{P} = \frac{M\omega}{Pl\delta},$$

and when  $Q > nP$

$$(n + 1) [\alpha] = \frac{M_w}{Pls}.$$

Since  $[a]$ ,  $[\alpha]$ , and  $n$  are constants, it is seen that the values of  $\frac{M_w}{Pls}$  expressed as a function of  $Q/P$  are represented by the co-ordinates of two straight lines cutting each other. When  $Q < nP$  or A is in excess the curve is a straight line inclined to both co-ordinates  $x$  and  $y$ ; when  $Q > nP$  or B is in excess, the specific rotation is independent of the excess of B and the curve runs parallel to one co-ordinate  $x$ . The author shows, however, that these two straight lines are merely tangents to the actual curve at the points where  $x = 0$  and  $x = \infty$ , because a further complication is introduced into the question by dissociation brought about by the solvent itself; the influence of this may be readily investigated theoretically, and the results are shown to be concordant by series of determinations of rotatory powers of pinene in various solvents and of solutions of sugar and potash in water. The calculated and observed numbers agree very closely indeed. The co-ordinates of the point of intersection of the two tangents to the curve give the composition of the compound of A and B; this, in the case of sugar and potash, consists of 2 mols. of the latter to 1 of the former.

The author concludes with a discussion of the work of Biot and Gernez on optically active solutions, and shows that the experimental results are in complete agreement with his own theoretical ones.

W. J. P.

**Fluorescence.** By E. BUCKINGHAM (*Zeit. physikal. Chem.*, **14**, 129—148).—Experiments were made to establish a connection between the phenomena of fluorescence and the ions present in the liquid. In the case of eosin, which contains acidic hydrogen, dilution increased the fluorescence; an addition of strong acids, that is, of hydrogen ions, caused it to diminish, as did also neutral salts if in sufficient quantity; strong alkalis also caused a decrease, probably owing to the formation of slightly dissociated salts. A few observations were made with  $\beta$ -naphthylaminedisulphonic acid,  $[(SO_3H)_2:NH_2 = 1:4:2]$ , and then a large number with quinine. This compound being a feeble base, the effect of alkalis on solutions of its salts should be to diminish the fluorescence which should be increased by acids and strongly dissociated neutral salts, and the observed results were as expected. The experiments also show that the bivalent quinine ion, as in  $Q_2SO_4H_2$ , is more strongly fluorescent than the univalent ions as in  $Q.HNO_3$ . Halogen ions exert a peculiar diminishing influence, which, although well marked and regular, the author is unable to explain. He considers, however, his results certainly indicate that fluorescence is an ionic phenomenon.

L. M. J.

**Electrolysis.** By O. WIEDEBURG (*Zeit. physikal. Chem.*, **14**, 174—180).—The paper contains a consideration of the question whether a certain maximum E.M.F. is required before electrolysis can be effected. The author considers that with any electromotive

orce (A) there corresponds a certain pressure ( $p$ ) of the gaseous product according to the equation  $A_1 - A_2 = c \log \frac{p_1}{p_2}$ , and hence is of opinion that by any electromotive force, however small, electrolysis is set up. The ratio of current to E.M.F. is given by a curve consisting of two straight lines connected by a short curve, approximately a hyperbola. Where the curve is very short, an apparent break occurs, the position corresponding with the maximum of polarisation.

L. M. J.

**Conductivity of Solutions.** By N. STRINDBERG (*Zeit. physikal. Chem.*, 14, 161—162).—The experiments of Arrhenius (*Abstr.*, 1892, 1038) and Holland (*Abstr.*, 1892, 1382) on the effect of a non-electrolyte on the conductivity of a solution, lead in both cases to the expression  $l = l_0 \left( 1 - \frac{ax}{2} \right)^2$  but the constant  $a$  differs greatly in the two sets of experiments. The author therefore redetermines this constant, using solutions of sodium and cuprous chlorides, with acetone and ethylic alcohol as the non-conductors. The results obtained agree well with those of Arrhenius, but differ from those of Holland to the extent of from 24 to 56 per cent.

L. M. J.

**Electrical Conductivity of some Salts in Ethylic and Methylic Alcohol.** By B. VÖLLMER (*Ann. Phys. Chem.*, [2], 52, 328—356).—The conductivities of the acetates and iodides of sodium and potassium, and of lithium chloride, dissolved in ethylic and methylic alcohols were measured, as also those of the chlorides of sodium and calcium, and the nitrates of silver and calcium, dissolved in ethylic alcohol.

The molecular conductivities increase with increasing dilution, and approach a limiting value for infinite dilution, except in the case of calcium chloride and of calcium nitrate. The limiting values for the molecular conductivities in methylic and ethylic alcohol solution may be obtained from those in aqueous solution by multiplication with a factor, in the first case about 0.73, and in the second about 0.34. It appears, therefore, that the conductivity decreases with the rising molecular weight of the solvent. The temperature coefficients increase with rising dilution, and for very dilute solutions the conductivity coefficients are practically the same as those for the viscosity of methylic and ethylic alcohols. Ostwald's dilution law is not applicable to the solutions examined, and from the conductivities it is not possible to calculate the rise in the boiling point of ethylic alcohol in its solutions, as it is with water.

H. C.

**Determination of Critical Temperatures by means of the Critical Index of Refraction.** By J. CHAPPUIS (*Compt. rend.*, 118, 976—977).—The author has employed the observation of interference bands as a means of following the changes in the refractive index of a liquefied gas near and at its critical temperature. The liquid is placed in a cylindrical cavity in a steel prism, provided with apertures covered with optically-worked glass plates and surrounded by



a liquid, the temperature of which can be controlled. Two beams of light produced by a pair of Jamin mirrors, starting from a Billet compensator, pass through the liquid in the prism, and through the surrounding bath, the sides of which are made of plates of optically-worked glass.

In the case of liquefied carbonic anhydride, the bands remain stationary and the refractive index is constant; beyond this temperature the bands fall and the refractive index increases rapidly. The curve of the indices at  $31.61^\circ$  shows a vertical tangent, and the intersection of this curve with the right line representing the index above this temperature is the critical point of the index. The results vary only between  $31.60^\circ$  and  $31.62^\circ$  (uncorr.), and the corrected value for the critical point as thus determined is  $31.40^\circ$ , which approaches closely to Amagat's value,  $31.35^\circ$ . C. H. B.

**Electrical Method for the Determination of Transition Points.** By E. COHEN (*Zeit. physikal. Chem.*, 14, 53—92).—If a voltaic element be formed by the immersion of similar electrodes in saturated solutions of the two forms of a substance capable of undergoing a transition change, then at temperatures above or below that of the transition, the current will flow in opposite directions, becoming *nil* at the transition temperature itself. This forms the basis of the method; such an element being placed in a thermostat, and the current measured at various temperatures, the null point being carefully determined. Details of the method and of the mode of preparing the element and the electrodes are given in the paper. The method is applicable to transition changes due to loss of water of crystallisation, formation of double salts, double decomposition, and polymorphism. The following changes are examined and the temperature determined:—

- (1.)  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$ .  $t = 32.8^\circ$ .
- (2.)  $\text{CdCl}_2 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{CdCl}_2 \cdot \text{H}_2\text{O} + \text{H}_2\text{O}$ .  $t = 34.1^\circ$ .
- (3.)  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} \rightleftharpoons \text{ZnSO}_4 \cdot 6\text{H}_2\text{O} + \text{H}_2\text{O}$ .  $t = \text{about } 42^\circ$ .
- (4.)  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{MgSO}_4 \cdot 7\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{MgSO}_4 \cdot 4\text{H}_2\text{O} + 13\text{H}_2\text{O}$ .  
 $t = 20.8^\circ$ .
- (5.)  $2\text{MgSO}_4 \cdot 7\text{H}_2\text{O} + 2\text{NaCl} \rightleftharpoons \text{MgNa}_2(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O} + \text{MgCl}_2 \cdot 6\text{H}_2\text{O} + 4\text{H}_2\text{O}$  (good results were not obtainable).

The author points out that the method has the advantages of accuracy and speed, but is only applicable to conductors, whilst for some of these the preparation of the electrodes is a matter of very great difficulty. The paper concludes with a consideration of the method from the thermodynamical standpoint, the fundamental equation

$$E = W + T \frac{dE}{dt},$$

being applied for this purpose.

L. M. J.

**Thermal Changes involved in the Formation of Amido-Acids and of Nitriles.** By F. STOHMANN and H. LANGBEIN (*J. pr. Chem.*, [2], 49, 483—501).—The following values are given:—

	Heat of combustion. Cal.	Heat of formation. Cal.
Glycocine, $\text{NH}_2\cdot\text{CH}_2\cdot\text{COOH}$ .....	234.6	125.9
Diglycolamidic acid, $\text{NH}(\text{CH}_2\cdot\text{COOH})_2$	396.3	221.2
Triglycolamidic acid, $\text{N}(\text{CH}_2\cdot\text{COOH})_3$	560.0	314.5

It will be seen that the mean difference between the heats of combustion for each  $\text{CH}_2\cdot\text{COOH}$  group introduced is 162.7 Cal. If this be also the difference between the heat of combustion of glycocine and that of solid ammonia, the latter value must be 71.9 Cal. The heat of combustion of gaseous ammonia is 90.6 Cal., and the heat of vaporisation of ammonia is 5.4 Cal. The heat of liquefaction of ammonia is not known, but a value for this which would reduce the heat of combustion to 71.9 Cal. can hardly be entertained as probable. Ammonia may stand in the same relationship to glycocine as that which has been shown to exist between formic and acetic acids and between oxalic and malonic acids; that is, ammonia may be more energetic than glycocine. The heat of combustion of hypothetical liquid ammonia devoid of chemical energy may be taken at 90.6 —  $(5.4 + 12.3) = 72.9$  Cal., for the heat of neutralisation of aqueous ammonia by aqueous hydrochloric acid is 12.3 Cal. On the basis of this value for ammonia, the author calculates the thermal values for the formation of glycolamidic acids by the interaction of ammonia and acetic acid, hydrogen being eliminated. The following conclusion may be drawn:—A hydrogen atom which enters into combination with a nitrogen atom effects a smaller increase of energy than when it enters into combination with a carbon atom (compare the variation in the heat of combustion produced by a methyl group under the same circumstances, *Abstr.*, 1892, 6; 1893, ii, 362). It can also be shown from the author's figures that more energy must be supplied for the formation of a compound in which a carbon atom is attached to a nitrogen atom, than is necessary when the carbon atom is attached to another carbon atom. Thus it happens that the substitution of  $\text{CH}_2\cdot\text{COOH}$  for H increases the heat of combustion by 162.7 Cal. when the H is attached to nitrogen, and by 150.9 Cal. when it is attached to carbon.

The thermal changes concerned in the conversion of amines into amido-acids are next considered, and passing to the nitriles the following figures appear:—

	Heat of combustion. Cal.	Heat of formation. Cal.
Diglycolamidic nitrile, $\text{C}_4\text{H}_4\text{N}_3$	590.8	—42.3
Triglycolamidic nitrile, $\text{C}_6\text{H}_4\text{N}_4$	846.2	—75.2

The thermal changes involved in the formation of the nitriles from the acids, and in the hydrogenation, hydrolysis, and formation of the nitriles are also considered.

A. G. B.

**Salt Formation in Alcoholic Solutions.** By C. M. VAN DEVENTER and E. COHEN (*Zeit. physikal. Chem.*, 14, 124—128).—The

authors extend their previous experiments (Abstr., 1890, 553; 1892, 262) to the neutralisation, by an acid, of sodium dissolved in mixtures of water and alcohol. In the case of hydrogen chloride, the heat of neutralisation diminishes from 100 per cent. to about 90 per cent. alcohol, increasing however with additional water content. A similar result obtains when the solution is neutralised by hydrogen bromide, but with acetic acid no minimum results, the value continuously increasing on addition of water. The authors explain these results by the assumption that three kinds of reaction occur—(1),  $\text{HCl} + \text{NaC}_2\text{H}_3\text{O} = \text{NaCl} + \text{C}_2\text{H}_3\text{O}$  (undissociated); (2),  $\text{HCl} + \text{NaOH} = \text{NaCl} + \text{H}_2\text{O}$  (undissociated); and (3),  $\text{H/Cl} + \text{Na/OH} = \text{Na/Cl} + \text{H}_2\text{O}$  (dissociated). In the case of the halogen acids, the heat of neutralisation is smallest for the second class, but with acetic acid, for the first class. They point out finally the importance of extended accurate observations where minima occur, in order to obtain data of the thermal effects for undissociated compounds.

L. M. J.

**Corresponding Solutions.** By G. TAMMANN (*Zeit. physikal. Chem.*, 14, 163—173; compare this vol., ii, 224, 268).—The author has previously shown that the thermal expansion of a solution at ordinary pressure corresponds with that of the solvent at a pressure  $\Delta k$ . Some cases of mixed solutions are examined, thus the values for  $\Delta k$  in the case of various solutions of potassium and sodium chlorides are given, and the expansion corresponding with the mean  $\Delta k$  is calculated, and found in most cases to agree well with the observed expansions of the mixed solutions. The concentration of solutions of the same salts, at which the values of  $\Delta k$  are equal, are also given, and found to agree well with Bender's "corresponding volumes; similar data being also given for the chlorides of lithium, barium, and ammonium. Such solutions should exhibit no volume alteration on mixing. Only in a few cases, however, are corresponding solutions also isohydric, examples of such cases being the carbonates and sulphates of sodium and potassium, in which the corresponding solutions are equimolecular. The sp. gr. of a mixture of equal quantities of these solutions therefore is the mean of the sp. gr. of the components, whilst they all exert the same effect in lowering the temperature of maximum density.

L. M. J.

**Determination of the Reduction of the Freezing Points of Solutions.** By A. PONSOT (*Compt. rend.*, 118, 977—980).—Regarding the freezing point of an aqueous solution as the temperature at which it is in equilibrium with ice, the author brings the solution in contact with an excess of finely-divided ice, agitates the mixture in a vessel carefully protected from radiation, reads the constant temperature, and pours off the liquid and determines its composition. The advantages claimed are that the liquid can contain no ice in superfusion, no correction is necessary for the concentration, and the temperature that has to be read off is stationary. A detailed description of the apparatus employed is given; the vessel containing

the solution is surrounded on all sides by jacketed cylinders containing mixtures at temperatures approximating to  $0^{\circ}$ . C. H. B.

**Relation between Depression of the Freezing Point and Osmotic Pressure of Solutions.** By C. DIETERICI (*Ann. Phys. Chem.* [2], 52, 263—274; compare this vol., ii, 228).—In answer to Arrhenius, the author admits the greater accuracy of Juhlin's observations on the vapour pressures of ice and water at temperatures below  $0^{\circ}$  as compared with those of Fischer, but still maintains that no strict proportionality exists between the depression of the freezing point and the osmotic pressure of solutions. The theoretical relationship existing between these two quantities is deduced, and it is shown that the assumption hitherto made, that the heat of dilution of dilute solutions is so small that it may be neglected, is incorrect.

H. C.

**Variations in the Viscosity of Fused Sulphur.** By J. BRUNHES and J. DUSSY (*Compt. rend.*, 118, 1045—1046).—The viscosity of fused sulphur at first decreases, like that of other liquids, as the temperature rises. The rate of transpiration increases from the melting point to a point between  $156^{\circ}$ — $157^{\circ}$ ; it then diminishes very rapidly, and at  $162^{\circ}$  it has become so viscous that it cannot be forced through a tube 1 mm. in diameter, even by the pressure of a column of mercury 700 mm. high. At higher temperatures, a change in the opposite direction takes place, and may be regarded as a second fusion.

At  $156^{\circ}$ , the rate of transpiration of the sulphur is 1.796 that at  $115.5^{\circ}$ . The rate of transpiration at  $115.5^{\circ}$  is 0.0518 and at  $156^{\circ}$  0.093 that of water at  $25.5^{\circ}$ .

C. H. B.

**Dissociation of Water.** By W. NERNST (*Zeit. physikal. Chem.*, 14, 155—156).—The author points out that, in the determination of the electrolytic dissociation of water by Ostwald (*Abstr.*, 1893, ii, 365), the difference of potential between the acid and base employed must not be neglected. He calculates this to be about 0.065 volt, and hence finds the dissociation to be  $0.8 \times 10^{-7}$ .

L. M. J.

**Dissociation of Saline Hydrates and Analogous Compounds.** By H. LESCEUR (*Ann. Chim. Phys.* [7], 2, 78—117).—A continuation of the author's previous experiments (*Abstr.*, 1893, ii, 364). Determinations of the tension of dissociation of several chlorides, bromides, and iodides are given, and from these data, as well as, in some case, by direct analysis, the existence of the following hydrates is established.  $\text{MgCl}_2 + 8\text{H}_2\text{O}$  (only obtained on one occasion; crystallises in long, silky fibres);  $\text{MgCl}_2 + 6\text{H}_2\text{O}$ ;  $\text{MgCl}_2 + 4\text{H}_2\text{O}$ ;  $\text{ZnCl}_2 + 2\text{H}_2\text{O}$ ;  $\text{CdCl}_2 + 4\text{H}_2\text{O}$ ;  $\text{CdCl}_2 + \text{H}_2\text{O}$ ;  $\text{FeCl}_2 + 6\text{H}_2\text{O}$ ;  $\text{FeCl}_2 + 4\text{H}_2\text{O}$ ;  $\text{FeCl}_2 + 2\text{H}_2\text{O}$ ;  $\text{FeCl}_2 + \text{H}_2\text{O}$ ;  $\text{Fe}_2\text{Cl}_6 + 12\text{H}_2\text{O}$  (yellow);  $\text{Fe}_2\text{Cl}_6 + 8\text{H}_2\text{O}$  (red). The following peculiarity of the yellow hydrate, which has been noticed by Berzelius, is without parallel; thus, instead of efflorescing in the air, it deliquesces, losing its water. The existence of the hydrates to be mentioned was also established:  $\text{CuCl}_2 + 3\text{H}_2\text{O}$ ;  $\text{CuCl}_2 + 2\text{H}_2\text{O}$ ;  $\text{CuCl}_2 + \text{H}_2\text{O}$ . Cuprous chloride is anhydrous; when agitated with water, it is converted into cuprous

oxide, but the yellow substance, which Wöhler believed to be the intermediate oxychloride, is simply a mixture of cuprous chloride and cuprous oxide.  $\text{BaBr}_2 + 2\text{H}_2\text{O}$ ;  $\text{BaBr}_2 + \text{H}_2\text{O}$ ;  $\text{MgBr}_2 + 6\text{H}_2\text{O}$ ;  $\text{MgBr}_2 + \text{H}_2\text{O}$ ;  $\text{ZnBr}_2 + \text{H}_2\text{O}$ ;  $\text{CdBr}_2 + 4\text{H}_2\text{O}$ ;  $\text{MnBr}_2 + 4\text{H}_2\text{O}$ ;  $\text{MnBr}_2 + \text{H}_2\text{O}$ ;  $\text{FeBr}_2 + 2\text{H}_2\text{O}$ ;  $\text{FeBr}_2 + \text{H}_2\text{O}$ ;  $\text{Fe}_2\text{Br}_6 + 6\text{H}_2\text{O}$ ;  $\text{Fe}_2\text{Br}_6 + 3\text{H}_2\text{O}$ ;  $\text{NaI} + 4\text{H}_2\text{O}$ ;  $\text{LiI} + 6\text{H}_2\text{O}$ ;  $\text{BaI}_2 + 6\text{H}_2\text{O}$ ;  $\text{MnI}_2 + 6\text{H}_2\text{O}$ ;  $\text{MnI}_2 + 4\text{H}_2\text{O}$ ;  $\text{MnI}_2 + 2\text{H}_2\text{O}$ ;  $\text{MnI}_2 + \text{H}_2\text{O}$ ;  $\text{FeI}_2 + 2\text{H}_2\text{O}$ ;  $\text{FeI}_2 + \text{H}_2\text{O}$ . The lower hydrates are, in general, better defined by their tensions of dissociation than the higher hydrates; these latter, by successive dehydration, pass gradually into lower hydrates. The tension of dissociation alone is not, therefore, as Debray believed, sufficient to indicate the existence of a hydrate.

The following table shows the results obtained by saturating with hydrogen chloride a saturated solution of the chlorides; it would seem that only those aqueous solutions having a greater tension at  $20^\circ$  than 8.5 mm. are precipitated by hydrogen chloride.

Initial compound.			Product precipitated by HCl.	
	Maximum tension of the saturated solution at $20^\circ$ .	Tension of dissociation at $20^\circ$ .		Tension of dissociation at $20^\circ$ .
	mm.	mm.		
$\text{BaCl}_2 + 2\text{H}_2\text{O}$ ..	About 15.45	About 3	$\text{BaCl}_2 + \text{H}_2\text{O}$ ..	Very small.
$\text{KCl}$ .....	" 13.55	Nil	$\text{KCl}$ .....	Nil.
$\text{NH}_4\text{Cl}$ .....	" 13.40	Nil	$\text{NH}_4\text{Cl}$ .....	Nil.
$\text{NaCl}$ .....	" 13.10	Nil	$\text{NaCl}$ .....	Nil.
$\text{CdCl}_2 + 4\text{H}_2\text{O}$ ..	" 12.20	About 10.5	$\text{CdCl}_2 + \text{H}_2\text{O}$ ..	Below 2.0 mm.
$\text{SrCl}_2 + 6\text{H}_2\text{O}$ ..	" 11.50	" 5.6	$\text{SrCl}_2 + 2\text{H}_2\text{O}$ ..	1.8 "
$\text{CuCl}_2 + 3\text{H}_2\text{O}$ ..	" 9.80	" "	$\text{CuCl}_2 + 2\text{H}_2\text{O}$ ..	Below 2.0 "
			green	
$\text{CoCl}_2 + 6\text{H}_2\text{O}$ ..	" 9.03	" 4.0	$\text{CoCl}_2 + 2\text{H}_2\text{O}$ ..	Very small.
			blue	
$\text{NiCl}_2 + 6\text{H}_2\text{O}$ ..	" 8.60	" 4.6	$\text{NiCl}_2 + 2\text{H}_2\text{O}$ ..	"
			yellow	
$\text{FeCl}_2 + 6\text{H}_2\text{O}$ ..	" "	" "	$\text{FeCl}_2 + 4\text{H}_2\text{O}$ ..	"
			green	
$\text{MnCl}_2 + 4\text{H}_2\text{O}$ ..	" 8.00	" 3.8	$\text{MnCl}_2 + 2\text{H}_2\text{O}$ ..	"
			white	
$\text{MgCl}_2 + 8\text{H}_2\text{O}$ ..	" 10.90	" "	$\text{MgCl}_2 + 4\text{H}_2\text{O}$ ..	Below 2 mm.
$\text{MgCl}_2 + 6\text{H}_2\text{O}$ ..	" 5.75	" 1.8	No precipitate	
$\text{Fe}_2\text{Cl}_6 + 12\text{H}_2\text{O}$ ..	" 6.50	" "	"	
$\text{CaCl}_2 + 6\text{H}_2\text{O}$ ..	" 5.40	" 2.3	"	
$\text{ZnCl}_2 + 2\text{H}_2\text{O}$ ..	Below 2.00	" "	"	

A. R. L.

**Rate of Diffusion of some Electrolytes in Alcohol.** By W. KAWALKI (*Ann. Phys. Chem.*, [2], 52, 300—327).—The results of the author's experiments on the rate of diffusion of electrolytes in alcohol

(this vol., ii, 308) are given in a series of tables, and the following conclusions are drawn from them.

The rate of diffusion increases as the concentration of the initial solution is diminished, the increase becoming more and more marked as the concentration decreases. With very small initial concentrations, the values calculated for the diffusion coefficient  $k$  from the determination of the concentrations of the different layers of the diffusate are not found to correspond with one another, although greater regularity is observed when the initial concentrations are high. This behaviour is probably due to convection currents in the dilute solutions, which disturb the regular course of the diffusion. The ratio of the diffusion coefficient in aqueous solution  $k'$  to that in alcoholic solution  $k$  is constant for any one salt, and practically independent of the concentration. It is also approximately equal to the ratio of the molecular conductivities for solutions of infinite dilution, as the following table of comparative values shows.

	$k'/k$ .	$\lambda'_\infty/\lambda_\infty$ .
NaI .....	2.72	2.62
LiCl .....	3.09	3.07
KOAc .....	2.52	2.92
NaOAc .....	2.31	2.50
KI .....	3.08	2.60
AgNO <sub>3</sub> .....	3.12	3.00

From this it appears that the rate of motion of the ions in water is about three times greater than in alcohol. The absolute values of the ionic velocities cannot be calculated from the author's results, but comparative values are obtainable, which accord with conclusions drawn from the electrolytic dissociation theory.

H. C.

### Absorption of Hydrogen by Water and Aqueous Solutions.

By P. SICINER (*Ann. Phys. Chem.*, [2], 52, 275—299).—The author has determined the absorption coefficient of hydrogen by water and a number of aqueous solutions of different concentrations. For water at 15°, the value 0.01883 was obtained, and the values of the

$m =$	1.	2.	3.	4.	5.	6.
LiCl .....	1574	1325	1121	949	—	—
KNO <sub>3</sub> .....	1524	1276	1076	—	—	—
AlCl <sub>3</sub> .....	1511	1221	993	810	667	550
KCl .....	1502	1217	996	820	—	—
NaNO <sub>3</sub> .....	1496	1201	984	808	667	542
CaCl <sub>2</sub> .....	1493	1195	958	780	635	510
NaCl .....	1478	1144	880	699	573	—
MgSO <sub>4</sub> .....	1451	1120	856	659	499	—
ZnSO <sub>4</sub> .....	1446	1113	852	667	510	—
Na <sub>2</sub> SO <sub>4</sub> .....	1370	991	710	—	—	—
K <sub>2</sub> CO <sub>3</sub> .....	1338	967	700	508	372	273
Na <sub>2</sub> CO <sub>3</sub> .....	1340	967	699	—	—	—
Cane sugar .....	1280	731	—	—	—	—

absorption coefficients for the solutions examined are given in the table.

In this table,  $m$  represents the number of gram-equivalents per litre of the solution, and the absorption coefficients have been multiplied by  $10^5$ . The author also gives a table of the values of the equivalent depression of the absorption coefficient  $\phi = (0.01883 - \beta)/m$ , where  $\beta$  is the absorption coefficient of the solution of concentration  $m$ . Attention is called to the almost identical values obtained for  $\text{MgSO}_4$  and  $\text{ZnSO}_4$ , and for  $\text{K}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3$ , the latter case being the more striking, as coincidence is not observed in the case of the other pairs of sodium and potassium salts examined. H. C.

### Physical Properties of Hydrated and Anhydrous Compounds.

By S. SURAWICZ (*Ber.*, 27, 1306—1316).—The author shows, by a general comparison of a large number of anhydrous compounds with the same substances in the hydrated condition, that the anhydrous compounds crystallise in systems of higher symmetry than the hydrated. Thus, in the case of the chloride, bromide, and iodide of sodium, the anhydrous salt is cubic, but the salt crystallising with  $2\text{H}_2\text{O}$  is, in each case, monoclinic. Hydration is attended, therefore, with a diminution in crystallographic symmetry, and a consequent considerable change in the thermal, optical, and many other chemical and physical properties. Among the latter may be reckoned a decrease in specific gravity and hardness, and an increase in specific volume, as comparison of anhydrous and hydrated compounds shows.

There are a certain number of exceptions to the above rule, some of which, however, are, as the author shows, only apparent. Cases of complete exception are  $\text{NaHSO}_4$ , triclinic, and  $\text{NaHSO}_4 + \text{H}_2\text{O}$ , monoclinic, and the bromo-derivatives of anhydroecgonine, which are monoclinic in the anhydrous, and tetragonal in the hydrated, state.

H. C.

### Speed of Reduction of Ferric Chloride by Stannous Chloride.

By L. KAHLENBERG (*J. Amer. Chem. Soc.*, 16, 314—323).—The well-known reaction between ferric and stannous chlorides proceeds slowly enough at zero to admit of study from the standpoint of chemical dynamics. By a series of carefully conducted experiments, the author has proved that the reaction follows the law of Guldberg and Waage fairly well.

In accordance with this law, the speed of the reduction of ferric chloride by an equivalent proportion of stannous chloride is expressed by the equation

$$\frac{dx}{dt} = c(a - x)^2,$$

in which  $a$  represents the amount of substance present at the outset,  $x$  the amount of substance changed during the time  $t$ , and  $c$  a constant depending on concentration, temperature, etc.

Free hydrochloric acid at first favours the reaction, but if more be added, the reaction is sensibly interfered with towards the end.

L. DE K.

**Reaction-velocities.** By J. E. TREVOR and F. L. KORRINGH (*Zeit. physikal. Chem.*, 14, 149—150).—In the inversion of cane sugar by an acid, the molecular concentration increases, and there should, therefore, be a corresponding variation in the boiling point and other properties dependent on the molecular concentration. By observations, therefore, of the increase in the boiling point at various stages of the inversion, the reaction-velocity may be determined according to the equation  $\frac{1}{t} \log \frac{z}{z-x} = ka$ , where  $z$  is the total increase,  $x$  that after time  $t$ , and  $a$  the concentration of the hydrogen ions. Results for 13 observations extending over 85 minutes, when 90 per cent. of the sugar was inverted, gave results for  $k$  varying only to the extent of 3 per cent. L. M. J.

**New Method of Determining the Relative Affinities of certain acids.** By M. C. LEA (*Amer. J. Sci.*, [3], 47, 445—451).—A method of measuring affinities is described, which is based on the principle that the affinity of any acid is proportional to the amount of base which it can retain in the presence of a strong acid selected as a standard of comparison for all acids. Sulphuric acid is here taken as the standard, and its presence or absence in the free state is ascertained by means of the herapathite test (compare *Abstr.*, 1893, ii, 566). If we suppose that the quantity taken is always a gram molecule at a fixed rate of dilution, it is evident that 2 gram mols. of sodium hydroxide would exactly saturate it. If we now take a given acid, we may find that a quantity of its sodium salt corresponding with 3 gram mols. of sodium hydroxide will exactly extinguish the reaction of a gram molecule of free sulphuric acid. With still another acid, we find that a quantity of its sodium salt corresponding with 4 gram mols. of sodium hydroxide is needed to extinguish the sulphuric acid reaction. Then the affinity of the second acid is exactly twice as great as that of the first. Thus in the case of hydrochloric acid, there was required 29.37 gram mols. of sodium chloride to extinguish the reaction in 1 gram mol. of sulphuric acid. The quantity 27.37 gram mols. is the proportion of undecomposed sodium chloride that must remain in the solution in order that the sulphuric acid, may be completely converted into sodium sulphate. This number 27.37, therefore, represents the strength of the affinity of hydrochloric acid for sodium. But in order to compare acids of different basicities, it is convenient to refer them all to bibasic sulphuric acid, and therefore the above number must be halved. Hence 13.68 may be taken as the index of the affinity of hydrochloric acid in comparison with those of other acids determined in like manner.

In this way the numbers given for the following acids were obtained: succinic, 0.21; acetic, 0.14; citric, 0.53; pyrophosphoric, 0.926; tungstic, 0.2. The applicability of the method was a good deal restricted owing to the tendency of many acids to decompose the herapathite reagent. Without obtaining exact numbers, it was, however, found that chloric acid has the strongest affinity for bases of any known acid, and that the comparative affinity of nitric acid



has hitherto been placed somewhat too high. Taking hydrochloric acid as 100, nitric acid scarcely exceeds 75. Qualitative experiments show that extremely feeble acids, such as hippuric and salicylic, are able to take a certain quantity of base, even from so strong an acid as sulphuric, setting free a recognisable quantity of the latter acid. Carbonic anhydride, however, even under pressure, does not liberate any portion of sulphuric acid from sodium sulphate.

In order to obtain true comparative results by the above method, it is necessary to use the sulphuric acid always at exactly the same dilution, and to add the dry salt to it. The affinity of sulphuric acid for water is, indeed, a most important factor in all determinations of this nature, as the following case illustrates. When 4 c.c. of normal sulphuric acid are added to 40 c.c. of normal sodium nitrate, not a trace of free sulphuric acid can be detected in the liquid. But when, instead of 4 c.c. of normal sulphuric acid, 40 c.c. of decinormal acid are used, although the quantities of acid and salt are exactly the same, the result is quite different, as free sulphuric acid then exists in the solution, and is abundantly indicated by the herapathite test.

H. C.

**Graphochemical Calculations.** By E. NICKEL (*Zeit. physikal. Chem.*, 14, 93—104).—An application of the author's methods to nitrogenous compounds of the general formula  $C_nH_mN_p$  (compare Abstr., 1892, 1158; 1893, ii, 119; this vol., ii, 235). L. M. J.

**Isomorphism.** By J. W. RETGEES (*Zeit. physikal. Chem.*, 14, 1—52, (compare Abstr., 1891, 146, 1151; 1892, 1048; 1893, ii, 193; this vol., ii, 85).—Elements and simple inorganic compounds crystallise mostly in the regular and hexagonal systems, 85 per cent. of the elements, 88 per cent. of diatomic compounds, and 53 per cent. of triatomic compounds obeying this rule; complex inorganic and organic compounds, on the other hand, form crystals belonging chiefly to the rhombic and monoclinic systems. The author points out that owing to this connection between crystallographic form and chemical simplicity, many compounds are only apparently and not really isomorphous, and contests the isomorphism of numerous compounds, such as lead, silver, and cuprous sulphides; mercuric and cupric sulphides; sulphides and arsenides or antimonides; whilst the isomorphism of sulphur and tellurium is also regarded as doubtful. The influence of chemical simplicity, however, extends only to form and not to miscibility, which the author therefore regards as the test of isomorphism. The frequent agreement of the crystallographic forms of metals, and their oxides or sulphides is also due to this cause, and not to any peculiar influence of the metal. The author does not consider the coloration of crystals by aniline and other dyes to be analogous to the formation of mixed crystals, but rather to a phenomenon akin to capillarity—the absorption of the dyes into the intermolecular spaces. The paper concludes with a discussion of the probable constitution of the plagioclase feldspars. L. M. J.

**Fractional Precipitation.** By T. PAUL (*Zeit. physikal. Chem.*, 14, 105—123).—If a mineral acid is added to a saturated solution of

an organic salt, a quantity of the organic acid is formed, and may be precipitated, the quantity being calculable if the solubility and dissociation data are known. A number of such data obtained experimentally, are given, and then the results of experiments performed with single acids. In this case the quantity precipitated is given by the equation  $(S - l - u)(H - l - u) = C$ , where  $S$  is the number of the acid radicles,  $H$  the number of hydrogen atoms,  $l$  the undissociated acid, and  $u$  the number of molecules precipitated. The acids examined were orthiodobenzoic, cinnamic, and paratoluic, and in each case the agreement between observed and calculated results was very good. The author points out also that the method could be used in the converse way to determine the dissociation of the acid. In the case of a mixture of two acids, two equations are necessary. If both acids are precipitated, there are

$$\begin{aligned} (1.) \quad & (S - l - u_1)(H - l_1 - u_1 - l_2 - u_2) = C_1 \\ (2.) \quad & (S - l - u_2)(H - l_1 - u_1 - l_2 - u_2) = C_2, \end{aligned}$$

whilst if one acid alone is present to saturation and is precipitated,  $u_1 = 0$ , and  $C_1 = k_1 l_1 v$ . This second case is first examined in the cases of mixtures of metabromobenzoic and orthotoluic acids; orthiodobenzoic and cinnamic acids; and orthiodobenzoic and paratoluic acids, close agreement with calculated numbers being in each case obtained. For the experiments on the precipitation of both acids, a large number of mixtures of iodobenzoic, toluic, cinnamic, and anisic acids were employed; the results, although not as concordant as in the previous cases, were still satisfactory. It is possible, the author points out, by the proper addition of the mineral acid to almost completely separate the pure acids from a mixture of their salts.

L. M. J.

**Sedimentation and Dye-absorption.** By O. LEHMANN (*Zeit. physikal. Chem.*, 14, 157—160).—Many compounds if dissolved in a liquid containing finely suspended material induce a precipitation of the particles, whilst in the case of colouring materials the dyes may also be precipitated. The action of a large number of compounds in causing the deposition of the carbon in Indian ink is recorded, and the author considers that the effect appears to depend on the formation around the particle of a layer of the dissolved material, so that the weight of the particles becomes so great that they can no longer remain suspended. The effect of thickening the solution is to retard the sedimentation, and the effects in this direction of different compounds are given.

L. M. J.

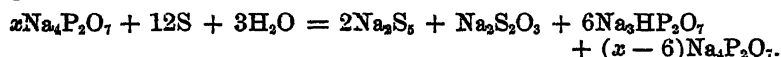
**A Continuous Automatic Mercury Air-pump for Chemical Purposes.** By G. W. A. KAHLBAUM (*Ber.*, 27, 1386—1394).—For a detailed description and figure of the pump, reference must be made to the original paper. The pump consists of two parts: a Sprengel pump, and an apparatus in which the mercury that flows away from the Sprengel is sucked up by the current of air induced by a water-pump. It is thus sucked up in the form of short columns, separated by spaces of rarefied air, and as the total height of this composite column can be much greater than that of the barometer, it is possible

in this manner to raise the mercury to such a height that it will flow back into the top of the Sprengel for further use there. The modification of the pump described is intended for use in vacuum-distillation; the distillation-apparatus is evacuated as far as possible with the water-pump, and then the pressure is reduced to 1 mm. with the mercury-pump. This last diminution of pressure is very advantageous; for instance, whilst a reduction of pressure from 760 to 50 mm. only lowers the boiling point of benzyl alcohol by 80°, a reduction from 10 to 1 mm. lowers it by 32°.

C. F. B.

## Inorganic Chemistry.

**Reaction of Sulphur and of the Halogens with Normal Sodium Pyrophosphate.** By T. SALZER (*Arch. Pharm.*, 231, 663—667).—Girard (*Compt. rend.*, 56) stated that when sulphur is boiled with an aqueous solution of normal sodium pyrophosphate, orthophosphoric and thiosulphuric acids are formed. The author has studied the reaction between sulphur and normal sodium pyrophosphate in aqueous solution, and finds that no orthophosphoric acid is produced, but that the reaction occurs in the sense of the following equation, where  $x$  depends on concentration, temperature, and pressure:



The halogens react with an aqueous solution of sodium pyrophosphate in a similar manner, the products being sodium bromide, sodium hypobromite, and trisodium hydrogen pyrophosphate, much normal sodium pyrophosphate being left unattacked. A. G. B.

**Action of Potassium Hydrogen Arsenite on the Salts of the Metals.** By C. REICHARD (*Ber.*, 27, 1019—1036).—The author has investigated the action of acid potassium arsenite,  $\text{K}_2\text{O} \cdot 2\text{As}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , on a number of metallic salts in dilute aqueous solutions. The following table exhibits the results obtained, the formulæ ascribed to the various arsenites having, in all cases, been established by analysis.

Composition.	Mode of preparation.	Properties.	Previous description.
$\text{Hg}_2\text{O} \cdot \text{As}_2\text{O}_3 \dots$	From $\text{HgNO}_3 \dots \dots \dots$	Yellowish mass, decomposing in light	Borzelius.†
$2\text{CuO} \cdot \text{As}_2\text{O}_3 \dots$	„ $\text{CuSO}_4^* \dots \dots \dots$	Green powder. . . . .	Bloxam.
$2\text{CdO} \cdot \text{As}_2\text{O}_3 \dots$	„ $\text{CdSO}_4^* \dots \dots \dots$	White, non-crystalline powder	—
$2\text{HgO} \cdot \text{As}_2\text{O}_3 \dots$	„ $\text{HgCl}_2^* \dots \dots \dots$	Yellowish-white mass, decomposing in light	Borzelius.†

Composition.	Mode of preparation.	Properties.	Previous description.
$2\text{PbO}, \text{As}_2\text{O}_3 \dots$	From $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2^*$ .....	White .....	$\text{PbO}, \text{As}_2\text{O}_3$ by Filhol† as being formed in this way.
$3\text{Au}_2\text{O}, \text{As}_2\text{O}_3 \dots$	„ $\text{AuCl}_3^*$ .....	Purple-red powder; blackens when heated or exposed to light	—
$3\text{Ag}_2\text{O}, \text{As}_2\text{O}_3 \dots$	„ $\text{AgNO}_3^*$ .....	Yellow microscopic needles; decomposes in light	Obtained by many authors.
$3\text{PbO}, \text{As}_2\text{O}_3 \dots$	„ $2\text{PbO}, \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$	White .....	Streng; Kühn.
$3\text{MgO}, \text{As}_2\text{O}_3 \dots$	„ $\text{MgSO}_4^*$ .....	White powder .....	Stein.
$3\text{ZnO}, \text{As}_2\text{O}_3 \dots$	„ $\text{ZnSO}_4^*$ .....	White crystalline mass	Bloxam.
$5\text{SnO}_2, 2\text{As}_2\text{O}_3 \dots$	„ $\text{SnCl}_4^*$ .....	Yellowish-white mass	Berzelius.†
$5\text{TiO}_2, 2\text{As}_2\text{O}_3 \dots$	„ $\text{TiOSO}_4^*$ .....	White crystalline substance	—
$\text{PtO}_2, \text{As}_2\text{O}_3 \dots$	„ $\text{PtCl}_4^*$ .....	} Light yellow masses	{ Simon.†
$\text{PdO}_2, \text{As}_2\text{O}_3 \dots$	„ $\text{PdCl}_4^*$ .....		
$\text{UO}_2, \text{As}_2\text{O}_3 \dots$	„ $\text{UO}_2(\text{NO}_3)_2$ .....		
$\text{Fe}_2\text{O}_3, \text{As}_2\text{O}_3 \dots$	„ $\text{FeCl}_3^*$ .....	Rust-yellow powder..	—
$\text{Al}_2\text{O}_3, \text{As}_2\text{O}_3 \dots$	„ $\text{Al}_2(\text{SO}_4)_3^*$ .....	White substance ...	Thorey.†
$\text{Cr}_2\text{O}_3, \text{As}_2\text{O}_3 \dots$	„ $\text{Cr}_2(\text{SO}_4)_3^*$ .....	Dark green mass, soluble in KOH	—
$\text{FeO}, \text{As}_2\text{O}_3 \dots$	„ $\text{FeSO}_4$ .....	Greenish-white substance; turns brown in the air	—
$\text{BaO}, \text{As}_2\text{O}_3 \dots$	„ $\text{Ba}(\text{NO}_3)_2$ .....	White substance, soluble in much water	—
$3\text{CoO}, 2\text{As}_2\text{O}_3 \dots$	„ $\text{Co}(\text{NO}_3)_2^*$ .....	Amethyst - coloured powder	} Girard.
$3\text{NiO}, 2\text{As}_2\text{O}_3 \dots$	„ $\text{Ni}(\text{NO}_3)_2^*$ .....	Light green substance	
$3\text{CaO}, 2\text{As}_2\text{O}_3 \dots$	„ $\text{CaCl}_2^*$ .....	{ White powders, soluble in much water	
$3\text{SrO}, 2\text{As}_2\text{O}_3 \dots$	„ $\text{Sr}(\text{NO}_3)_2^*$ .....		
$3\text{MnO}, 2\text{As}_2\text{O}_3 \dots$	„ $\text{MnCl}_2^*$ .....	White, becoming pink to brown in the air	Stein.
$3\text{SnO}, 2\text{As}_2\text{O}_3 \dots$	„ $\text{SnCl}_2^*$ .....	Yellowish-white mass, decomposed by acids and alkalis with separation of free arsenic	Berzelius.†

\* Indicates that the respective acids were set free during the formation of the new salt.

† In these cases the salts had not been analysed by the earlier investigator.

A. H.

**Salts of Rubidium.** By H. EEDMANN (*Arch. Pharm.*, 232, 3—36).—Chemically pure rubidium salts are best prepared by making use of ferric rubidium alum, which can be obtained quite free from potassium salts, since ferric potassium alum is not only very soluble in water but has the property of dissociating in solution. The author has prepared pure specimens of a large number of rubidium salts, and

has studied their physical properties, more particularly the density, refractive index, and solubility in water. The following compounds have been examined:— $\text{RbHSO}_4$ ;  $\text{Rb}_2\text{S}_2\text{O}_7$ ;  $\text{Rb}_2\text{SO}_4$ ;  $\text{RbAl}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ ;  $\text{RbFe}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ ;  $\text{RbCr}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ ;  $\text{RbBF}_4$ ;  $\text{Rb}_2\text{Co}(\text{NO}_2)_6 + \text{H}_2\text{O}$ ;  $\text{RbMgCl}_2 + 6\text{H}_2\text{O}$ ;  $\text{RbClO}_4$ ;  $\text{RbClO}_3$ ;  $\text{RbIO}_3$ ;  $\text{RbHI}_2\text{O}_6$ ;  $\text{RbI}$ ;  $\text{RbICl}_4$ .

Rubidium alum melts at  $105^\circ$ ; its refractive index is 1.45648 at  $20-23^\circ$ . The sp. gr. of ferric rubidium alum is 1.9520;  $n = 1.48225$  at  $21-22^\circ$ , corresponding with the molecular refraction 135.63. For rubidium iodide  $n = 1.6262$ , the molecular refraction = 38.45 and the sp. gr. is 3.447.

Mercuric iodide dissolves in a solution of rubidium iodide, a yellow double salt being formed. When this salt is treated with water, mercuric iodide is set free, since its solution is stable only when excess of rubidium iodide is present. Rubidium iodotetrachloride (Wells and Wheeler, *Abstr.*, 1893, ii, 68) is dissociated by heat into rubidium chloride and iodine trichloride; its solution liberates iodine from potassium iodide, and on adding ammonia to it, a black precipitate of iodide of nitrogen is at once formed. A concentrated solution of the salt attacks metals, dissolving even gold and platinum. The author concludes by discussing the physiological action of rubidium iodide, and its application in pharmacy. M. O. F.

**Barium Nitride.** By BERTHELOT and MATIGNON (*Ann. Chim. Phys.*, [7], 2, 144).—*Barium nitride*,  $\text{BaN}_2$ , is obtained by treating a solution of ammonium nitride with an equivalent weight of barium hydroxide, and evaporating the solution under diminished pressure in the cold; it thus furnishes beautiful crystals. The gram-molecular heat of dissolution at  $19.8^\circ$  is  $-7.8$  Cal. A. R. L.

**Copper Bromide.** By P. SABATIER (*Compt. rend.*, 118, 980—983).—Dilute solutions of cupric bromide are blue, but when concentrated by evaporation at the ordinary temperature they become emerald green, then dark green, and finally red-brown, the solution depositing bulky, black, monoclinic prisms of the anhydrous bromide  $\text{CuBr}_2$ . This salt is highly deliquescent; heat of dissolution at  $12^\circ = +7.9$  Cal., a value which agrees well with Thomsen's (8.2 Cal.).

In winter the brown solutions sometimes deposit long, brilliant, bottle-green, monoclinic needles of the hydrate  $\text{CuBr}_2 \cdot 4\text{H}_2\text{O}$ . It is very deliquescent; heat of dissolution at  $7.5^\circ = -1.5$  Cal.

It follows that—

$\text{CuBr}_2 \text{ sol.} + 4\text{H}_2\text{O sol.} = \text{CuBr}_2 \cdot 4\text{H}_2\text{O sol.}$  develops  $+3.7$  Cal.

Like hydrated metallic chlorides the heat of hydration of which is less than 2 Cal. per molecule of water, the hydrated cupric bromide effloresces in dry air, and loses all its water; its behaviour when freely exposed to the atmosphere depends on the degree of humidity of the latter. Dehydration takes place even in solution, the green liquid becoming temporarily brown and opaque when heated.

Alcohol dissolves the anhydrous bromide, forming highly opaque, yellowish-red solutions.

When a minute quantity of cupric bromide is added to concentrated

hydrobromic acid, an intense purple coloration is produced, in consequence, probably, of the formation of a hydrobromide of the bromide. This reaction is more sensitive than either the ferrocyanide or sulphide reaction, and will detect 0.0015 milligram of copper in a drop of a solution of the bromide, but the hydrobromic acid must be concentrated. A mixture of potassium bromide with a saturated solution of phosphoric acid can be used instead of hydrobromic acid.

C. H. B.

**The Molecular State of Calomel Vapour.** By W. HARRIS and V. MEYER (*Ber.*, 27, 1482—1489).—After enumerating the experiments of previous observers, the authors describe some new ones which they have made. A sheet of gold leaf, dipped for a moment in calomel vapour, becomes amalgamated; if held there longer the coating of mercury evaporates. A thermometer immersed in rapidly evaporating calomel indicated 357°, a temperature very nearly that of boiling mercury. The rate of volatilisation of calomel at different temperatures was approximately determined, and the vapour density at 448° and at 518° was found, by V. Meyer's method, to correspond with the constitution  $\text{HgCl}$ , or  $\text{Hg} + \text{HgCl}_2$ . The same vapour density was obtained with a mixture, in these proportions, of mercury and corrosive sublimate, and, on cooling, calomel was deposited in the apparatus. When calomel, contained in a porous cell, was heated at 465° inside a test-tube, mercury vapour was found to have diffused through the porous walls, and condensed on the walls of the test-tube, while some mercuric chloride was found inside the porous cell. Further, if a rod of potash, previously heated to 240—260°, is dipped into the vapour of calomel at the same temperature, it is *immediately* covered with a yellow coat of mercuric oxide, whereas a black coat of mercurous oxide only begins to turn yellow at this temperature after the lapse of some 20 seconds. All these facts indicate that calomel as such is not volatile, but that its "vapour" is completely dissociated into mercury and mercuric chloride.

C. F. B.

**Calomel.** By E. DIVERS (*J. Soc. Chem. Ind.*, 13, 108—111).—The author concludes from his experiments on a Japanese method of manufacturing a peculiar form of calomel that in this case the calomel is formed by a reaction between mercury vapour, oxygen, and hydrogen chloride gas,  $4\text{Hg} + 4\text{HCl} + \text{O}_2 = 4\text{HgCl} + 2\text{H}_2\text{O}$ , and that the reaction takes place at a temperature near to the boiling point of mercury, and much below that at which calomel volatilises. The calomel cannot be the result of true sublimation, but of precipitation as fast as it is formed from the three gaseous substances which give rise to it, and its not reaching its subliming temperature is the explanation of its freedom from corrosive sublimate.

L. T. T.

**Crystallisation of Gold in Hexagonal Forms.** By A. LIVERSIDGE (*Chem. News*, 69, 172—173).—When precipitating a solution containing 15 grains of sodium aurochloride,  $\text{AuCl}_3 \cdot \text{NaCl} \cdot 2\text{H}_2\text{O}$ , to 15 ozs. of water, by means of freshly fractured fragments (i) of copper pyrites, (ii) of the graphitic casing from an auriferous vein, or (iii) of zinc blende, the gold was observed to be deposited in very small, bril-

liant, lustrous prisms arranged in fan-like groups, or in six-rayed stellate tufts, or in some instances in the form of minute hexagonal plates. Many sulphides precipitate the gold as an ochre-coloured, lustreless, mammillated film, whilst cubical crystals are obtained by precipitation with ferrous sulphate, oxalic acid, &c. This is, however, as the author points out, not the first time that hexagonal crystals of gold have been observed.

D. A. L.

## Mineralogical Chemistry.

**Condition of Gold in Quartz and Calcite Veins.** By A. LIVERSIDGE (*Chem. News*, 69, 162—163).—Removing gangue and associated minerals by chemical means—hæmatite, spathic iron, and calcite by hydrochloric acid; mispickel, &c., by nitric acid, or by roasting and subsequent treatment with hydrochloric acid; quartz, &c., by hydrofluoric acid—enabled the author to examine the condition of the residual gold. Generally, the gold from hard matrices like quartz is found to be non-crystalline, but occurs as irregular films, plates, threads, or masses more or less connected together, and when the gangue is dissolved away forms a spongy or cavernous mass; such gold has been obtained from Mount Morgan stalactitic hæmatite, from New Caledonia Reef (Queensland) quartz, and from many other specimens of gold quartz; on the other hand, crystalline gold is encountered in the weathered and decomposed parts of quartz reefs, in what are now cavities, and in soft matrices such as the gold-bearing calcites of the New South Wales gold mines and the Gympie mines of Queensland, the serpentine of Gundagai, and Lucknow, and some of the clear quartz from New Zealand. The larger the fragments of gold, the less the tendency to crystalline form. The author has also observed crystalline form in alluvial gold from Fairfield, New England, N. S. W., it was not water-worn, and so had not travelled far from the parent reef.

D. A. L.

**Gold Ores of California.** By H. W. TURNER (*Amer. J. Sci.*, [3], 47, 467—473).—As is well known, gold in California occurs chiefly in quartz veins, usually in the slate series of the Sierra Nevada. It occurs, however, in a great variety of rocks, and associated with very different minerals. The occurrences grouped geologically are enumerated by the author, those cited being veins in the auriferous slate series, and veins in the granite. He instances the occurrence of gold in albite, in calcite with barytes and with cinnabar, and in rhyolite with quartz.

B. H. B.

**Artificial Zinc Oxide and Wurtzite.** By H. TRAUBE (*Jahrb. f. Min. Beilage*, 9, 147—153).—1. Zinc oxide as a metallurgical product has frequently been described. The author has, however, collected at the smelting works in Upper Silesia some well-developed

crystals of zinc oxide of unusual form and colour. The crystals described are colourless, yellow, green, and dark brown. The axial ratio is considerably affected by the presence of small quantities of foreign elements, as is shown by the following table.

Colour.	Composition.	$a : c$ .
Colourless.....	Pure	1 : 1.60770
Yellow .....	Traces of CdO, FeO	1 : 1.60817
Green .....	0.38 FeO, traces MnO	1 : 1.66835
Brown.....	0.48 FeO, 0.27 MnO, traces CdO	1 : 1.64026

2. Wurtzite as a metallurgical product has been described by Förstner and by Stahl. The author has found this substance in very large quantities in the lead slags of the Friedrichs works at Tarnowitz. Its composition was found to be as follows.

Fe.	Zn.	Mn.	Pb.	S.	Total.
0.81	66.02	trace	trace	32.79	99.62

B. H. B.

**Composition of Wavellites and Turquoises.** By A. CARNOT (*Compt. rend.*, 118, 995—998).—Four specimens of wavellite had the following composition, the fluorine being determined by the author's method (*Abstr.*, 1892, 911).

	F.	P <sub>2</sub> O <sub>5</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO and MgO.	H <sub>2</sub> O.	Clay and quartz.	Total.
A.	1.90	32.38	37.03	0.40	traces	27.72	0.43	99.86
B.	2.79	33.40	37.44	0.64 (FeO)	traces	26.45	—	100.72
C.	2.09	33.55	36.83	0.36	traces	27.53	0.16	99.86
D.	1.81	22.07	34.82	1.40	traces	26.16	3.75	100.01

A, from Cork, Ireland, was in greyish mamelons, and dull grey radiating fibres; B, from Clonmel, Ireland, was similar in structure, but yellowish-green and dull green in colour; C, from Chester, U.S.A., was in small, white, elongated stalactites; and D, from Garland, Arkansas, was in greyish, globular masses, composed of radiating fibres. The mean of the four analyses is

P <sub>2</sub> O <sub>5</sub> .	Al <sub>2</sub> O <sub>3</sub> .	F.	H <sub>2</sub> O.
33.20	37.38	2.17	27.25

which corresponds with the formula  $2(\text{Al}_2\text{O}_3, \text{P}_2\text{O}_5) + \text{Al}_2(\text{O}_3, \text{F})_4 + 13\text{H}_2\text{O}$ .

Two specimens of oriental turquoise, one (E) from Persia, and the other (F) from Nevada had the following composition.

	P <sub>2</sub> O <sub>5</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CuO.	CaO.	Clay.	H <sub>2</sub> O.
E.	29.43	42.17	4.50	—	5.10	—	0.21	18.59
F.	30.38	44.82	5.32	0.22	7.40	traces	—	11.86

28—2



Fluorine is absent. The composition of the mineral corresponds only very approximately with the formula  $P_2O_5.(Al_2,Cu_2,Fe_2)O_3 + Al_2O_3 + 5H_2O$ .

Two specimens of occidental turquoise or odontolite had the following composition: G, from Munster, Ireland, was greenish-blue, whilst H had the same colour but was uniform in tint.

	F.	P <sub>2</sub> O <sub>5</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	CO <sub>2</sub> .	Clay.	Loss on heating.
G.	3.02	43.46	22.59	6.45	20.10	traces	5.07	0.37	—
H.	3.45	41.27	17.71	5.80	24.72	0.99	5.60	0.18	1.20

Odontolite is not constant in composition, which is a natural result of the fact that it is an alteration product formed under a variety of conditions.

C. H. B.

**Analysis of Pele's Hair from Hawaii.** By A. H. PHILLIPS (*Amer. J. Sci.*, [3], 47, 473—474).—The author gives the following results of analyses of Pele's hair (I) and of a stalagmite (II) from the lava caves of Kilauea.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	P <sub>2</sub> O <sub>5</sub> .	CaO.	MgO.
I.	50.76	14.75	2.89	9.85	0.41	0.26	11.05	6.54
II.	51.77	15.66	8.46	6.54	0.82	—	9.56	4.95
			Na <sub>2</sub> O.	K <sub>2</sub> O.	Total.			
			I. 2.70	0.88	100.09			
			II. 2.17	0.96	100.89			

B. H. B.

**Beaver Creek Meteorite.** By E. E. HOWELL, W. F. HILLEBRAND, and G. P. MERRILL (*Amer. J. Sci.*, [3], 47, 430—435).—This meteorite fell between 3 and 4 p.m., May 26, 1893, near Beaver Creek, West Kootenai District, British Columbia. It is a typical aerolite of very pronounced chondritic structure with the usual fused black crust. Its unusual feature is that beneath the crust there is a slight oxidation for a distance of  $\frac{1}{2}$  in. to  $\frac{3}{4}$  in. Analysis shows the meteorite to be composed of 17.13 per cent. of nickel iron, 0.16 per cent. of magnetite, 5.05 per cent. of troilite, 37.23 per cent. of soluble silicates and phosphate, and 40.43 per cent. of insoluble silicates and chromite.

B. H. B.

## Physiological Chemistry.

**Acid in Protozoan Digestion.** By M. GREENWOOD and E. R. SAUNDERS (*J. Physiol.*, 16, 441—467).—The secretion of acid by protozoa as determined by litmus and alizarin sulphate has been mooted by other observers, especially by le Dautec.

In the experiments now recorded, acid indicators were admin-

istered in combination with food stuffs. The infusorian, *Carchesium polypinum*, and the plasmodia of certain mycetozoa were selected as subjects for the experiments. In the method of ingestion, the formation of vacuoles, and the exclusive digestion of proteids, the phenomena observed were closely similar to those previously recorded in rhizopods.

The ingestion of solid matter of whatever nature always stimulates the cell to secrete an acid fluid round it in a more or less extensive vacuole. This acid is, however, not a digestant, but delays digestion. The process of digestion is accompanied by a gradual and finally total disappearance of the acid.

From its behaviour to congo-red, the acid is judged to be free acid, and not carbonic acid.

W. D. H.

**Influence of Ferments occurring in Vegetables on the Nutrition of the Organism.** By H. WEISKE (*Zeit. physiol. Chem.*, 19, 282—284; compare this vol., ii, 286).—In certain vegetables, amylolytic, proteolytic, and other ferments occur. In order to prove whether these assist digestion in the animal organism, or at least increase the nutritive value of the food, rabbits were during one period fed on the raw vegetable (oats); and during another on the oats which had been heated to destroy the ferments. The intake and output of material were measured in the usual way, and the results were practically the same during both periods.

W. D. H.

**Red Blood Corpuscles of different Specific Oxygen Capacities.** By J. H. HALDANE and J. L. SMITH (*J. Physiol.*, 16, 468—475).—In relation to Bohr's work on this subject, it is here recorded that there are distinct differences, amounting sometimes to more than 20 per cent., in the specific oxygen capacity of different layers of corpuscles in centrifugalisated blood. But no relationship was found constant between this capacity and the layer, or the size, or specific gravity of the corpuscles.

W. D. H.

**Ground Substance of Connective Tissue.** By R. A. YOUNG (*J. Physiol.*, 16, 325—350).—The forms of connective tissue investigated were those that contain but few formed elements (cells and fibres), and a large amount of ground substance or matrix. The general results obtained may be briefly summarised as follows:—

1. The vitreous humour is extremely poor in solids containing only slightly over 1 per cent.; the intact vitreous shows a great resistance to the action of digestive juices or putrefaction.
2. The vitreous humour contains mucin, although in comparatively small quantities and very possibly as mucinogen. It has the reactions of a typical mucin, except that it is distinctly soluble in excess of acetic acid.
3. From the so-called membranes of the vitreous, distinct, although small, quantities of gelatin can be obtained.
4. The vitreous contains two other proteids, namely, a globulin coagulating at 75°, and an albumin coagulating about 80°.
5. Whartonian jelly yields large quantities of mucin in two forms,

one soluble, the other insoluble, in excess of acetic acid. This mucin is acid in reaction, and darkens on exposure.

6. It also yields two proteids, one like myosin coagulating at 56°, and an albumin coagulating at 84°.

7. The reducing product or gummoses obtained from funis mucin reduces Fehling's, but not Barfoed's reagent. It gives a brown, amorphous compound with phenylhydrazine, and yields no catechol on being heated with strong alkali.

8. Funis mucin is not digested by artificial gastric juice, but is readily digested by artificial pancreatic juice, and the products (mucin-albumose and peptone) yield, like the mucin from which they come, a reducing substance on heating with dilute mineral acid.

W. D. H.

**Chemistry of Muscle.** By A. WHITFIELD (*J. Physiol.*, 16, 487—490).—Myosin is a globulin, not a nucleo-albumin. It contains an appreciable amount of phosphorus in its molecule; on gastric digestion, it leaves only an insignificant residue, and this contains no phosphorus. It does not produce intravascular coagulation.

Muscle contains no nucleo-albumin. Proteoses (albumoses) and peptone are also absent.

W. D. H.

**Bone in Osteomalacia.** By M. LEVY (*Zeit. physiol. Chem.*, 19, 239—270).—The mineral constituents are less in the bones of osteomalacial patients than in normal bones. The relation  $6\text{PO}_4:10\text{Ca}$  of normal bone ash remains the same in osteomalacia. The diminution in the phosphate, therefore, proceeds *pari passu* with that of the carbonate.

Fresh normal bones treated with lactic acid lose much more carbonate than phosphate. Osteomalacia cannot, therefore, be explained by the presence of lactic or other free acid.

The organic constituents of the bone show in this disease no qualitative change. But the relative increase of marrow leads to an increase in the proportion of proteid to gelatin.

W. D. H.

**Development of Heat in Salivary Glands.** By W. M. BAYLISS and L. HILL (*J. Physiol.*, 16, 351—359).—From the experiments recorded, the conclusion is drawn that no development of heat can be directly determined in the submaxillary gland by any known method of measuring variations in temperature.

W. D. H.

**Formation of Glycogen.** By J. FRENTZEL (*Pflüger's Archiv.*, 56, 273—288).—Cremer states that pentoses increase the quantity of glycogen in the liver, not because they are themselves transformed into glycogen, but because they exercise a sparing influence.

The present research relates to the same question. It was found that by the use of strychnine, animals can be rendered glycogen-free. On giving xylose, it was found that no glycogen was subsequently discoverable.

Control experiments showed that glycogen was formed if other substances were administered that ordinarily give rise to glycogen either directly or by a sparing action.

W. D. H.

**Formation of Urea in the Liver.** By C. RICHET (*Compt. rend.*, 118, 1125—1128).—The liver continues to exhibit after its removal from the body, while the vitality of its cells lasts, the same chemical phenomena as while it is within the body. For instance, sugar is formed from its glycogen. The present research shows that the same is true for the formation of urea, and the opinion is advanced that this, like the formation of sugar, is due to a ferment action.  
W. D. H.

**Diastatic Ferment of the Liver.** By E. SALKOWSKI (*Pflüger's Archiv.*, 56, 351—354).—It is pointed out that the use of chloroform water, which destroys protoplasm but leaves enzymes intact, has been employed by the author previous to the appearance of Bial's paper (this vol., ii, 106). The result of this work coincides with that of Bial, that the conversion of glycogen into sugar is the result of a diastatic ferment action.  
W. D. H.

**Ferment Processes in Organs.** By H. SCHWIENING (*Virchow's Archiv.*, 136, 444—481).—In this communication a number of questions are taken up, the link connecting the various researches together being Salkowski's observation that chloroform water destroys living protoplasm and formed ferments, but is inactive on enzymes. Here, then, is a means of distinguishing in an organ undergoing changes after its removal from the body whether or not an enzyme is the cause of the change.

An organ is taken, divided into two parts, one of which (A) is subjected to the action of chloroform water, the other (B) boiled and sterilised; both are examined after the lapse of a certain time. In A the xanthine substances go completely, in B incompletely, into solution. If a liver is examined, A contains sugar, no glycogen, large quantities of leucine and tyrosine; it does not give the biuret reaction. In B there are only traces of sugar, abundant glycogen, and no leucine or tyrosine; it gives the biuret reaction. The acidity in the two cases is the same, but the amount of organic substances, nitrogen, and phosphoric anhydride that go into solution are greater in A than in B.

In the case of muscle, A gives no biuret reaction, but a weak reduction of Fehling's solution; whilst B gives a biuret reaction, but no reduction. In A the acidity is increased. In both, leucine and tyrosine are absent; there is no rise in the soluble organic substance, nitrogen, or phosphoric anhydride, as in the liver.

These results of Salkowski's are extended in the present paper, and the ferment action is termed auto-digestion.

The formation of sarcolactic acid after death is regarded as a vital phenomenon. The muscle forms acid not because it is dead or dying, but because it is still alive.

Experiments with chloroform water lend no support to the theory that the liver forms sugar from glycogen in virtue of the vital activity of its cells, but the presence of a ferment is considered necessary. Curiously enough, boiling does not inhibit the change of glycogen into sugar. This has been observed before, and the explanation con-

sidered most feasible is that the ferment is destroyed by heat, but that fresh ferment appears as the disintegration of the cells subsequently takes place.

W. D. H.

**Influence of Decomposition of Proteid on the Output of Neutral Sulphur.** By N. SAYELIEFF (*Virchow's Archiv.*, 136, 195—202).—An experiment relating to proteid metabolism was made on a dog. The intake in nitrogen was the same every day, but during four days in the middle of the research 200 c.c. of chloroform water was given with the food. This led to an increased output of nitrogen, and also of sulphur, in which the proportion of neutral sulphur to the total sulphur in the urine was increased.

W. D. H.

**Analyses of Milk.** By J. LEHMANN and W. HEMPEL (*Pflüger's Archiv.*, 56, 558—578).—The analyses relate chiefly to the ash associated with casein. The casein of cow's milk contains 7.2 per cent. of ash: this consists of  $\text{CaO}$ , 49.5;  $\text{MgO}$ , 2.4;  $\text{P}_2\text{O}_5$ , 47.0; and  $\text{SO}_3$ , 1.06 per cent. The elementary composition of casein is thus given: C, 50.86; H, 6.72; N, 14.63; P, 0.81; S, 0.72; ash, 6.47 per cent. The casein of woman's milk contains more sulphur (1.09 per cent.) and less ash (3.2 per cent.). The composition of milk is given thus:—

	Cows' milk.	Human milk.
Casein.....	3.0	1.2
Albumin.....	0.3	0.5
Fat.....	3.5	3.8
Lactose.....	4.5	6.0
Ash.....	0.7	0.2
Water.....	88.0	88.5

W. D. H.

**Influence of Cold Baths on the Excretion of Nitrogen and Uric acid.** By E. FORMÁNEK (*Zeit. physiol. Chem.*, 19, 271—281).—Cold baths naturally call on the organism for an increased production of heat, and the present research, carried out on human beings, shows that the increased metabolism falls in part on the proteids of the body. A single bath-day makes little or no difference, but a succession of these raises the total output of nitrogen slightly, and of uric acid very slightly. The average of 24 days which were normal or bathless gives *per diem* total output of nitrogen 14.88, and of uric acid 0.7025 grams. The average of seven days, on which two cold baths were taken, gives 15.46 and 0.7194 respectively.

W. D. H.

**Carbonic Oxide Poisoning.** By G. MARTEN (*Virchow's Archiv.*, 136, 535—547).—Five cases of poisoning by carbonic oxide are given, with clinical details. In all, the body temperature was elevated. As regards metabolism, the decomposition of proteid is enormously increased. There may be slight albuminuria. The pulse is like that of typhoid fever. The red corpuscles of the blood are increased considerably.

W. D. H.

**Action of Oxalates on Nerve and Muscle.** By W. H. HOWELL (*J. Physiol.*, 16, 476—486).—Irrigation of a nerve in frogs and terrapins by dilute solutions of sodium oxalate destroys its irritability towards electrical stimuli, without, however, killing it, as a well-marked demarcation current is present; which, however, more rapidly disappears than in normal nerve.

In a nerve muscle preparation, it is the motor end plates which are first affected. The suggestion is made that removal of calcium salts will explain the loss of irritability.

The loss of irritability in muscle is preceded by convulsive twitchings, and, contrary to the observations of Cavazanni, the oxalated muscle went in every case into *rigor mortis* sooner than a normal muscle.

W. D. H.

**Arrow Poisons.** By L. LEWIN (*Virchow's Archiv.*, 136, 82—126, 403—443).—This is a historical account of the subject of arrow poisons, together with some physiological experiments on animals, relating to their action; in some cases the source of the poison is given or guessed at; the question of the chemical substances present is hardly gone into, and in no case completely. The account of the different poisons used by various and numerous tribes shows that they vary considerably.

W. D. H.

## Chemistry of Vegetable Physiology and Agriculture.

**Formation of Resins and Ethereal Oils in Plants.** By A. TSCHIECH (*Ann. Agron.*, 20, 299—300; from *Jahrb. Wiss. Bot.*, 25, 370; *Bot. Centr.*, 57, 18).—The following products were examined. Sumatra and Siam benzoin (*Styrax benzoin*), Peru balsam (*Myroxylon pereiræ*), Tolu balsam, styrax (*Liquidambar orientalis*) and galbanum (*Ferula galbaniflua, rubicaulis, &c.*). When hydrolysed, they yield, on the one hand, aromatic (chiefly benzoic and cinnamic) acids, or alcohols, and a group of "resin alcohols" or "resinols," on the other. Benzoresinol,  $C_{18}H_{28}O_2$ ; resinotannol,  $C_{18}H_{26}O_4$ ; siareresinotannol,  $C_{18}H_{14}O_2$ ; peruresinotannol,  $C_{18}H_{20}O_5$ ; storesinol,  $C_{12}H_{18}O$ ; and galbaresinotannol,  $C_6H_{10}O$ , were obtained. The termination "tannol," signifies that the alcohols give the tannin reaction. Resin alcohols yield with aromatic acids, or with other alcohols, ethers which seem to be identical with the natural ethereal salts of resins.

Resins frequently contain free acids and alcohols, as well as ethers. The fact that the highly carbonaceous resins and essences are formed at the earliest period of the life of the plant, when all disposable matter is utilised in the building up of new tissues, would seem to indicate that these compounds have an important biological rôle.

N. H. M.

**Composition of the Cotton Plant.** By HURCHINSON and PATERSON (*Bied. Centr.*, 1894, 403—404).—The analyses of the plants were made at six stages of growth, and the first set were undertaken in 1890, when the plants grew on a dark grey loam overlying close clay; whilst in 1891 the soil was a porous, yellow loam; the main difference in the composition of the soils is to be found in the potash and lime,  $K_2O$  0.540,  $CaO$  0.255, in 1890, and  $K_2O$  0.34,  $CaO$  0.145, in 1891, but the ash constituents are vastly different.

1890.

	Crude protein.	Fat.	Carbo- hydrates.	Fibre.	Ash.	$SiO_2$ .	$Fe_2O_3$ .	$CaO$ .	$MgO$ .	$K_2O$ .	$Na_2O$ .	$P_2O_5$ .	$SO_3$ .
Roots.....	0.39	2.92	38.76	48.59	3.34	5.32	3.47	16.08	11.00	23.28	2.38	10.05	3.31
Stem.....	6.71	2.24	38.01	51.93	3.06	1.80	0.63	20.36	11.31	24.80	4.08	9.53	3.62
Leaves.....	21.62	7.84	41.52	14.49	14.53	3.13	0.90	35.66	7.86	12.60	1.64	9.31	6.71
Seed.....	21.09	9.07	29.68	33.73	5.68	2.01	1.50	10.10	8.15	37.92	4.04	19.26	6.81

1891.

	Crude protein.	Fat.	Carbo- hydrates.	Fibre.	Ash.	$SiO_2$ .	$Fe_2O_3$ .	$CaO$ .	$MgO$ .	$K_2O$ .	$Na_2O$ .	$P_2O_5$ .	$SO_3$ .
Roots.....	3.25	2.50	37.78	52.54	3.93	28.47	8.34	11.91	7.43	20.07	3.86	13.83	2.21
Stem.....	6.95	1.79	39.45	47.45	4.36	5.58	4.01	21.09	5.46	26.61	4.68	12.74	3.23
Leaves.....	18.60	9.86	49.06	10.56	11.92	4.10	2.20	34.22	7.64	15.99	2.08	14.38	8.16
Seeds.....	11.84	3.19	66.42	14.74	3.81	3.31	7.22	10.68	10.06	35.55	0.68	20.40	7.59

E. W. P.

**Seeds of "Chenopodium album L."** By G. BAUMERT and K. HALPERN (*Arch. Pharm.*, 231, 641—644).—These seeds are sometimes used as a substitute for rye. It will be seen from the following tables that, although the seeds are richer in nitrogenous matter and fat than is either rye or wheat, they contain a smaller total of digestible constituents. In rye or wheat flour the chenopodium betrays itself by its high content of ash and fibre.

*Composition of Seeds of Chenopodium album L.*

	Baumert and Halpern.		Erismann.	Kapustin.	Salmenew.	Mean.
	Seed.	Husk (Calyx leaves).				
	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.
Water .....	10·33	7·45	10·66	17·04	10·92	12·23
Nitrogenous matter*	13·94	12·25	18·88	15·75	17·60	15·29
Fat .....	6·97	2·86	6·28	5·88	6·93	6·51
Nitrogen-free extract	39·30	39·66	47·42	37·70	38·52	40·73
Fibre .....	25·68	17·93	16·52	17·58	21·45	20·31
Ash .....	3·88	19·85	5·24	6·05	4·58	4·94
*Containing proteins	12·56	9·91	—	—	—	—

Mean composition of	Water.	Ash.	Fibre.	Fat.	Nitrogenous matter.	N-free extract
Wheat (König) ..	13·65	1·81	2·53	1·75	12·35	67·91
Rye (König) ....	15·06	1·81	2·01	1·79	11·52	67·81
Chenopodium ...	12·22	4·94	20·31	6·51	15·29	40·73

A. G. B.

**Cacao Bean.** By H. BECKURIS (*Arch. Pharm.*, 231, 687—694).—The author gives a detailed account of the methods adopted for estimating the fat, theobromine, and starch in the cacao bean. The variations from the usual methods are in details alone, and can only be appreciated by reference to the original. Tables are given which show the analytical data obtained from 23 trade brands. The following table gives the maxima and minima of these data.

	Per cent.
Fat* .....	42·00—57·40
Theobromine .....	0·63—2·20
Starch .....	7·56—16·53
Ash .....	2·20—3·75

\* Chloroform extract, freed from dissolved theobromine by treatment with water.



Constants of fat:—

Melting point.....	30.0—36.5°
Melting point of fatty acids .....	48.5—53.0°
“Saponification number” .....	193—220
Iodine absorption.....	32.8—40.0

A. G. B.

**Henbane Seed Oil.** By H. SCHWANERT (*Arch. Pharm.*, 232, 130—136).—This oil consists chiefly of olein, with a small quantity of palmitin and traces of colouring matter; it is free from alkaloids. The iodine number by Gantter's process is 64.48, the Hübl method giving 156.25. The author attributes this discrepancy to the employment of mercuric chloride in the latter process.

M. O. F.

**Manuring with Phosphates, &c.** By MÄCKER (*Bied. Centr.*, 1894, 374—376).—The researches have extended over three years, and have been chiefly directed to the examination of the action of phosphates. It is an error to believe that the “after action” of a phosphatic manuring continues for so long, or is so intense as is generally supposed; and it is found that even in those soils richest in phosphates, the third crop begins to shrink in quantity.

With basic slag, the same amount of straw may be obtained as when superphosphate is used, but the yield of grain is far less, even to one-half as little, and doubling the amount of slag does not double the crop of grain; likewise in its after action basic slag is behind superphosphate. Bones only act well on soils already containing a fair supply of phosphates.

E. W. P.

## Analytical Chemistry.

**Estimation of Oxygen in the Blood.** By I. NOVI (*Pflüger's Archiv*, 56, 289—303).—Siegfried (*Archiv. Anat. Physiol. Physiol. Abth.*, 1890, 385) states that blood only gives up a part of its oxygen to sodium hyposulphite; more can be extracted by the air pump. The blood which has lost this portion of oxygen shows no trace of oxyhæmoglobin bands with the spectroscope, that which remains is in a compound called pseudohæmoglobin. The apparatus used by Siegfried has been modified by Schützenberger, and some more alterations are suggested in the present paper. The experiments recorded confirm Siegfried's main contention, but show that the amount of oxygen removable by his method varies considerably in different animals, and in the same animals under different conditions.

W. D. H.

**Estimation of the Strength of Sulphuric acid.** By H. D. RICHMOND (*Chem. News*, 69, 236).—The author has made a careful determination of the density of mixtures of weighed quantities of sulphuric acid and water, the results point to the correctness of a

table prepared from Pickering's results (Trans., 1890, 64 *et seq.*), Lunge and Isler's table (Abstr., 1891, 150) being found to be quite wrong.  
D. A. L.

**Estimation of Phosphorus in Iron, Steel, and Ores containing Arsenic.** By J. O. HANDY (*J. Amer. Chem. Soc.*, 16, 231—234).—The author has found that when testing iron by the molybdate process, the yellow, phosphatic precipitate nearly always contains more or less arsenic, although in the absence of phosphorus no precipitate is obtained at all. The precipitate may be freed from arsenic by dissolving it in 15 c.c. of dilute ammonia (1—6), diluting with water to 75 c.c., and, after heating to 75°, adding a mixture of 10 c.c. of nitric acid (sp. gr. 1.42) and 25 c.c. of Wood's molybdate solution. It is then washed with dilute nitric acid (1—100), dried, and weighed, or else titrated, as usual.  
L. DE K.

**Dudley's Method of estimating Phosphorus in Steel.** By O. S. DOOLITTLE and A. EAVENSON (*J. Amer. Chem. Soc.*, 16, 234—247).—The authors have, by a special process, reinvestigated the nature of the yellow phosphomolybdate precipitate, and confirmed the usually accepted statement that the ratio between phosphorus and molybdic acid must be taken as 1.792.

The means adopted for reducing the molybdic acid have a considerable influence on the results of the titrating process. The reduction should be carried out by dissolving the precipitate in dilute ammonia, adding granulated zinc and shot, and then boiling with excess of dilute sulphuric acid.

The authors also find that there is little danger of arsenic precipitating with the phosphorus if the iron solution is not heated above 32°.  
L. DE K.

**Comparison of Pemberton's Method of Estimating Phosphoric acid with the American Official Process.** By W. C. DAY and A. P. BRYANT (*J. Amer. Chem. Soc.*, 16, 282—283).—The agreement between the two methods is remarkably close. There is no exaggeration in Pemberton's statement, that a sample of phosphate may be analysed in some 30—40 minutes.  
L. DE K.

**Direct Estimation of Citrate Soluble Phosphoric acid.** By B. B. ROSS (*J. Amer. Chem. Soc.*, 16, 304—308).—Citric acid interferes with the precipitation of phosphoric acid with molybdate solution, and several devices have been proposed to remove it from the phosphatic solution. The author now recommends destroying it by imitating Kjeldahl's method, and operates as follows. After digesting the phosphate with 100 c.c. of the official citrate solution, 25 c.c. of the liquid is at once filtered into a dry vessel, preferably a burette, and, after cooling, an aliquot part is put into a digestion flask of 250—300 c.c. capacity, 15 c.c. of strong sulphuric acid is added, and the flask put on a piece of gauze over a moderately brisk flame. After about 8 minutes, foaming and darkening will set in; after further lapse of 3—4 minutes the foaming will cease. About 1 gram

of mercury is now added, and the digestion continued over a high flame; after about half an hour, a clear and almost colourless liquid will be obtained.

The solution is washed into a beaker, rendered slightly alkaline with ammonia, then acidified with nitric acid, and treated by the regular molybdate method. The test analyses are entirely satisfactory.

L. DE K.

**Recovery of Molybdic acid from Residues, and Remarks on Phosphoric acid Estimation.** By H. BOENTRÄGER (*Zeit. anal. Chem.*, 33, 341—343).—The whole of the filtrates, both acid and ammoniacal, from the phosphoric acid precipitates, are poured into a large flask containing ammonia. Pure molybdic acid separates in fine needles. The liquid is finally made nearly neutral, the precipitate collected on a filter, washed slightly, and pressed. It is then dissolved in the least possible quantity of ammonia, the solution rapidly filtered from silica and magnesia, diluted with water to a density of 1.11, and poured into an equal volume of nitric acid of 1.2 sp. gr., allowed to deposit for 24 hours, and the clear solution poured off for use.

The author, with Fresenius, adds fuming nitric acid to the ammoniacal solution of the yellow precipitate, until the precipitate produced no longer dissolves immediately. The magnesia mixture is added to the hot solution, and filtration commenced as soon as air bubbles rise from the pulverulent precipitate, which takes place in 1—2 hours. The precipitate is incinerated without removal from the filter, and Barthel's spirit lamp is strongly recommended for the purpose.

M. J. S.

**Estimation of Silica.** By A. CAMERON (*Chem. News*, 69, 171—172).—The author fused a sample of silica, containing 98.5 per cent.  $\text{SiO}_2$ , 0.1 of  $\text{Fe}_2\text{O}_3$ , 0.5 of  $\text{Al}_2\text{O}_3$ , 0.7  $\text{CaO}$ , and 0.2  $\text{MgO}$ , with fusion mixture decomposed with hydrochloric acid, evaporated to dryness in a porcelain basin, continuing the heating after the acid fumes were driven off, and then proceeded in the usual way, subsequently subjecting the filtrate to various treatments, including evaporating to dryness over a water bath and over a flame, with various strengths of sulphuric acid, or with hydrochloric acid, or in the presence of iron, of alumina, of calcium carbonate, or of organic matter. He finds that in all cases at least two evaporations are required to obtain all the silica from solution; that it is more effectually separated over the flame than over the water bath; that hydrochloric acid is as efficient as, and preferable to, sulphuric acid; that the admixtures make very slight difference to the purity of the silica, which was tested by treatment with hydrofluoric acid; and that repeated evaporations in the first instance show no advantage over the single evaporation.

D. A. L.

**Estimation of Impurities in Commercial Nickel.** By T. FLEITMANN (*Zeit. anal. Chem.*, 33, 335—338).—The most usual impurities are iron, copper, cobalt, zinc, and manganese. Not less than 5 grams of the metal is dissolved in aqua regia, and the solution

repeatedly evaporated with hydrochloric acid. From the filtered solution the iron is precipitated by cautious neutralisation with dilute sodium carbonate, addition of a drop of acetic acid and boiling. The precipitate is again dissolved and thrown down by ammonia, when any copper it may have contained will be separated. To the filtrate from the iron precipitate, a drop of hydrochloric acid is added, and then saturated hydrogen sulphide solution drop by drop until the copper is exactly precipitated. Then by passing hydrogen sulphide gas through the filtrate, the zinc is precipitated as sulphide, which is subsequently converted into carbonate. The filtrate is freed from hydrogen sulphide by boiling, and after neutralisation by sodium carbonate is treated at 60–80° with feebly alkaline sodium hypochlorite. The manganese comes down first as brown manganic oxide, then the cobalt as blackish-brown cobaltic hydroxide, and then a small portion of the nickel as deep black nickelic hydroxide, the commencement of the precipitation of the latter being indicated by the evolution of oxygen. The liquid is boiled and the precipitate collected, dissolved from the filter with hot hydrochloric acid, the solution heated to expel chlorine, the hydrochloric acid replaced by acetic acid, and the cobalt and nickel precipitated by hydrogen sulphide and separated by potassium nitrite, which can very well be accomplished when the proportion of nickel is first reduced as above. The manganese is found in the filtrate as acetate. Traces of arsenic, antimony, and tin would be found with the iron precipitate; lead with the copper.

M. J. S.

**Oxidation and Chemical Properties of Gases.** By F. C. PHILLIPS (*Amer. Chem. J.*, 16, 340–365; compare this vol., ii, 293, 294).—Acetylene forms the well-known metallic compounds. The soluble silver compound constitutes the most delicate test, and is also the best means of preserving acetylene, the copper compound being liable to oxidation. Acetylene is oxidised to carbonic anhydride at the ordinary temperature by osmic acid, calcium hypobromite, or a solution of potassium permanganate in concentrated sulphuric acid, and by iodic acid at 90°. The osmic acid is reduced to metallic osmium, the iodic acid to iodine; gold chloride is also reduced to metallic gold, and ferric chloride to ferrous chloride.

Allylene forms similar metallic compounds. The palladium compound is dark-brown, the silver compound white, the cuprous compound canary-yellow. Allylene is oxidised to carbonic anhydride by the same reagents as acetylene, and reduces gold and palladium to the metallic state. Unlike acetylene it does not precipitate ammoniacal silver nitrate. The formation of the silver compound constitutes the most delicate test.

Carbon oxysulphide may be separated and distinguished from hydrogen sulphide by means of dry mercuric oxide, copper carbonate, litharge or white lead spread on cotton-wool, with which substances it does not react. It reacts with solutions of metallic salts, the metallic sulphide and carbonic anhydride being formed. It is readily oxidised to carbonic anhydride and sulphuric acid by bromine water or acid permanganate.

Methylmercaptan may be separated from hydrogen sulphide by means of mercuric oxide, with which it combines only slowly. It forms compounds with many metals, mostly of different colour to the corresponding sulphides. The lead, copper, and silver compounds are yellow, the cadmium compound white. The metallic compounds are decomposed by hydrogen sulphide. Methylmercaptan is very stable towards oxidising agents. It is not oxidised even by a fused mixture of sodium carbonate and potassium dichromate or nitrate.

Methylic sulphide can be purified from hydrogen sulphide and methylmercaptan by means of an aqueous sodium hydroxide solution of lead hydroxide. The mercaptan may be recovered by heating the lead compound with dilute acid. The metallic compounds are all fairly soluble. Methylic sulphide is quite as stable towards oxidising agents as the mercaptan, and may be distinguished from the latter by means of the sparingly soluble palladium compound, which crystallises in microscopic, monoclinic prisms, and, unlike the corresponding compound from methylmercaptan, is readily soluble in hot water.

Nitrogen forms compounds with magnesium, lithium, and potassium.

Oxygen may be conveniently recognised in coal-gas and the like by passing the gas successively through caustic soda and manganous chloride solutions in closed vessels. When the air has been expelled, some of the soda is transferred to the manganese vessel. If oxygen is present, the resulting manganous hydroxide is oxidised to the brown hydrated peroxide. The test may be rendered still more delicate by the subsequent addition of potassium iodide and dilute sulphuric acid. Aqueous pyrogallol may be substituted for the manganous chloride.

JN. W.

**Estimation of Glycerol in Wine.** By H. D. PAXION (*Chem. News*, 69, 235—236).—10 c.c. of wine is treated with slaked lime, transferred drop by drop to an expanded piece of filter paper, dried at the ordinary temperature, extracted with absolute alcohol in a Soxhlet apparatus, the extract evaporated in a flask, redissolved in ether alcohol, filtered, evaporated, and the residue dried and weighed. There is less loss of glycerol than when other methods of evaporation are employed, whilst the glycerol appears to be quite as pure.

D. A. L.

**Butter Fat.** By A. PIZZI (*Stat. Sper. Agrar.*, 25, 101—118; compare this vol., ii, 75).—The following method was employed for fractionating the glycerides of butter by slow cooling. The butter (400 grams) was melted in a long tube, 8 cm. in diameter, placed in a thermostat kept at 80°. In about an hour, the melted butter was stirred with a glass rod and left for half an hour; it was then filtered through a hot filter into a weighed beaker. The amount of fat obtained in the experiment recorded was 234.89 grams. The beaker was now covered and placed in the bath heated at 80°; after 4 hours the gas was turned out and the whole left for two days, by which time the butter had cooled to the ordinary temperature of the laboratory (26.2°) and was partly solid. The liquid portion was removed by

filtration and finally by placing the solid substance on tiles. Two experiments made in 1891 and 1892 gave the following percentage results:—

	Solid glycerides.	Liquid glycerides.
1891 .....	35.20	64.80
1892 .....	32.90	67.10

Butter fat was further fractionated by cooling down to different temperatures and separating the solid matter each time. The temperatures employed were (1) 26.2°, (2) 21.2°, (3) 17.0°, (4) 12.4°, (5) 11.0° and (6) 6.5°. A table is given showing the sp. gr. of the liquid portion at each temperature, the melting and solidifying points of the solid matter, the volatile acids (as c.c. N/10 alkali) and the iodine numbers of both solid and liquid matter. As regards density, there is an increase as the temperature at which the separation was made decreases. The melting points decrease from 44° (solid separated at 26.2°) to 10.5° (solids separated at 6.5°), the melting point of the original being 36°. The volatile acids increased from 28.05 to 34.10 in the liquid, and from 19.91 to 31.02 in the solid portion. The iodine numbers also show a great increase. On comparing the amounts of volatile acids of the liquid fat of different periods, the results show a very regular difference between each period (except the period 4—3). Thus, the difference in amounts in periods 2 and 1 is 1.76; in 3 and 2, 1.76; in 5 and 4, 1.98; and in 6 and 5, 1.76.

The solid fat which separated at 26.2°, when magnified 170 diameters was seen to consist of globules without particular interest. It did not show any colours with polarised light. The solids obtained at 21.2—12.4°, consisted of little globules, whilst the fat which separated at 11—6.5 consisted of cruciform rosettes which showed in a remarkable degree the Newtonian colours.

N. H. M.

**Estimation of Fat in Bread.** By M. WEIBULL (*Zeit. angew. Chem.*, 1895, 199—202).—The author's process (Abstr., 1893, ii, 197) having been tried, unsuccessfully, by Polenske, a large number of fresh experiments are communicated, showing the method to be perfectly trustworthy, but it is necessary to work exactly as follows:—

4 grams of new, or 3 grams of stale bread is put into a 70 c.c. beaker and covered with 30 c.c. of water, and 10 drops of dilute sulphuric acid. The whole is boiled, very carefully at first, over a very small straight flame for at least  $\frac{3}{4}$  hour, some hot water being occasionally added to rinse the sides of the beaker. Towards the end the liquid is evaporated to about half its bulk. While still warm, the contents are carefully neutralised with powdered marble, a large excess being avoided. The mixture is then spread over a piece of filter paper (such as is used in Adam's milk process) and any liquid remaining in the beaker is removed by means of a piece of cotton-wool which is then put on to the filter paper. The latter, resting on iron gauze, is first dried for 10 minutes at 100°. The paper is now rolled into the usual shape, and then dried for 3—4 hours at 100—103°. After this it is placed in a Soxhlet's apparatus and

extracted at least 60 times with pure ether; this will generally take between four and five hours.  
L. DE K.

**A New Method of Analysing Fats and Resins.** By P. C. McILHINEY (*J. Amer. Chem. Soc.*, 16, 275—278).—The author's process is based on the fact that the unsaturated constituents of fats combine with bromine forming simple additive products, whilst resins and rosin cils are acted on with formation of hydrogen bromide.

The following reagents are required:—N/3 solution of bromine in carbon tetrachloride; N/10 solution of sodium thiosulphate; N/10 solution of potassium hydroxide. Not more than 1 gram of the sample of suspected oil is dissolved in 10 c.c. of carbon tetrachloride in a bottle of 500 c.c. capacity provided with a carefully-ground glass stopper. An accurately-measured excess of the bromine solution is added, the bottle tightly stoppered and placed in a dark place for 18 hours. The bottle is cooled with ice to form a partial vacuum, and a piece of wide rubber tubing, about  $1\frac{1}{2}$  inch long, is slipped over the lip of the bottle so as to form a well about the stopper. This well is filled with water and the stopper carefully lifted when the water will be sucked into the bottle and dissolve any hydrobromic acid. When 25 c.c. of water has been added, the bottle is well shaken and 20 c.c. of a 20 per cent. solution of potassium iodide is added. The liberated iodine is now estimated with thiosulphate, a check experiment being made as usual, and the difference is calculated to the percentage of bromine. The contents of the bottle are now transferred to a separating funnel, and the aqueous portion is separated, filtered through a cloth filter, and titrated with potassium hydroxide with methyl-orange as indicator. This gives the acidity which may be conveniently expressed in percentages of free bromine. Multiplied by 2 and deducted from the *total* bromine the bromine *addition* number is obtained.

The latter is *nil* for rosin and rosin oils, but reaches the high figures of 102.88 and 103.92 for fresh and boiled linseed oils. The author is engaged in the investigation of a large number of oils and resins by means of this method, and hopes to furnish new analytical *data* for their commercial analysis.  
L. DE K.

**Acetone in Urine.** By E. SALKOWSKI (*Pflüger's Archiv.*, 56, 339—343).—In estimating acetone in urine by conversion into iodoform, the possibility that acetone might in part originate from carbohydrates in the urine during distillation was suggested. On putting this to the test of experiment, it was found that sugar in urine does give rise to a substance which gives many of the reactions of acetone, but which is an aldehyde, probably acetaldehyde.

W. D. H.

**Chenopodine. Detection of Chenopodium Seed in Flours.** By G. BAUMERT and K. HALPERN (*Arch. Pharm.*, 231, 648—653).—The evidence as to the injurious property of chenopodium is conflicting, and the existence of an alkaloid in the plant has been disputed. Engelhard claimed to have isolated an alkaloid from chenopodium

which he termed chenopodine. Reinsch sought to show that this base was identical with leucine. The authors find that both their predecessors were dealing with betaine, and the name chenopodine must therefore be expunged from chemical literature. Since betaine is not poisonous, the toxic action which chenopodium seed undoubtedly exerts in "Hungerbrot" must be attributed to some other constituent; neither a saponin compound nor oxalic acid is present, but there is a small quantity of an ethereal oil in the seed which has not been physiologically tested. Paracholesterol was detected in the ether extract of the seed. The rose or deep red colour which an alcoholic hydrochloric acid extract, made by some hours' digestion of chenopodium flour at a temperature somewhat above the normal, exhibits may serve for microscopical detection of the seed (compare this vol., ii, 363).  
A. G. B.

**The Decomposition of Proteids, &c., by Alkaline Hydroxides.** By V. VEDRÓDI (*Zeit. anal. Chem.*, 33, 338—340).—From the observation that tobacco freed from nicotine yields ammonia when distilled with soda (Abstr., 1893, ii, 504), the author was induced to attempt the estimation of the nitrogen in proteids, etc., by this reaction, but in 12 hours' distillation, albumin, casein, gluten, and gelatin had yielded only 77, 60, 44, and 76 per cent. respectively of their total nitrogen.  
M. J. S.

**The Analysis of Malt.** By J. A. MILLER (*J. Amer. Chem. Soc.*, 16, 353—360).—The author, having tried several methods, thinks the following process is the best. 50 grams of the sample is put into a weighed copper beaker, and mixed with 200 c.c. of water at 40°, which temperature is gradually increased to 60°. After 20 minutes' digestion, a few drops of the liquid is tested for starch, and should this be present the temperature is raised 1° every two minutes until it has completely disappeared. After cooling, water is added to make 450 grams total contents. After thoroughly mixing, the mass is thrown upon a plaited filter, but the first half of the filtrate is thrown back once more upon the filter. After collecting as much as possible of the filtrate, its sp. gr. is taken by means of the Westphal balance. From this gravity the percentage given by Schultze's tables is ascertained, and that number multiplied by 8.75, which gives the percentage of dry extract from the malt.

The author has experimentally proved that the extract cannot be accurately determined by evaporation and drying at 105° owing to the serious decomposition of maltose at that temperature. This, of course, applies to the estimation of extract in beers. Drying the extract at 70—75° is impracticable, except for scientific purposes.

L. DE K.

**Quantitative Separation of the Amorphous Nitrogenous Organic Compounds in Beer Wort.** By H. SCHJERNING (*Zeit. anal. Chem.*, 33, 263—299).—The precipitate produced by soda solution in beer wort contains a small proportion of the total nitrogen, that by baryta or stannous chloride a larger proportion, that by lead acetate still more, a further increase with ferric acetate, and the



largest amount with phosphomolybdic acid or uranium acetate. For all these reagents the author has investigated the conditions for the maximum precipitation, as well as the corrections for solubility in the filtrate and wash-waters. The substance precipitable by soda is also completely thrown down by baryta, phosphomolybdic acid, and uranium acetate, but not by the other reagents. The absolute baryta precipitate (the substance precipitable by baryta after that by soda has been removed) is identical with the stannous chloride precipitate, and is also precipitable by lead acetate, ferric acetate, phosphomolybdic acid, and uranium acetate. The lead acetate precipitate is also completely precipitable by ferric acetate, phosphomolybdic acid, and uranium acetate. The ferric acetate precipitate is completely thrown down by phosphomolybdic acid and uranium acetate. The phosphomolybdic acid precipitate contains all the constituents precipitable by the other reagents, together with all the ammonia in the wort. The uranium acetate precipitate contains the same nitrogenous constituents as the phosphomolybdic, with the exception of such of the ammonia as is not thrown down by the soda. The nitrogen in the soda precipitate is entirely in the form of ammonium magnesium phosphate, accompanied by other magnesium and calcium phosphates, magnesium saccharate, and traces of a lactate. Only about one-fourth of the ammonia in the wort is contained in this precipitate. The examination of the precipitates by the other reagents is, as yet, incomplete, but the absolute baryta precipitate seems to be an acid product of the splitting up of diastase, analogous to nuclein, and for which the provisional name "Denuclein" is suggested; the absolute lead precipitate seems to contain either unaltered mucedin or an acid albumin, the absolute ferric acetate precipitate to contain a propeptone, and that with uranium or phosphomolybdic acid actual peptones. A partial confirmation of this view results from the agreement of the sum of the lead and ferric acetate precipitates with that obtained by saturating the wort with magnesium sulphate.

M. J. S.

**Peptone in Urine.** By E. SALKOWSKI (*Chem. Centr.*, 1894, i, 658; from *Centr. Med. Wiss.*, 1894, 113—115).—Addition of commercial peptone to the extent of more than 0.01 per cent. to urine can be detected as follows:—50 c.c. of urine is acidified with 5 c.c. of hydrochloric acid, and precipitated with phosphotungstic acid and warmed. The precipitate, which aggregates on standing, is collected in a filter, washed twice with water, and then mixed with 8 c.c. of water and 0.5 c.c. of sodium hydroxide solution, by which means a deep blue coloration is developed. By warming in a test-tube, this becomes a dirty grey-yellow, and then on the addition of a few drops of a 1 per cent. solution of copper sulphate gives the usual biuret reaction. Urine rich in mucin, or albumin, must be freed from these in the usual way before applying the test.

W. D. H.

## General and Physical Chemistry.

**Line Spectrum of Oxygen.** By B. HASSELBERG (*Ann. Phys. Chem.* [2], 52, 758—761).—The author refers to the measurements of the line spectrum of oxygen by *fig.* (this vol., ii, 265), criticises their accuracy, and draws attention to similar measurements made by Neovius (*Bih. K. Sven. Vet. Akad. . . .*, 1891). H. C.

**Absorption Spectra of Solution of Cupric Bromide in Hydrobromic acid.** By P. SABATIER (*Compt. rend.*, 118, 1144—1146).—A solution of cupric bromide in hydrobromic acid, containing only 0.5 gram of copper per litre, is almost opaque (compare this vol., ii, 304), and the absorption spectrum can only be observed with very thin layers or in much more dilute solutions. With a freshly-prepared solution of 0.150 gram of copper in 780 grams of hydrobromic acid the transmission of light is distinct in the red, decreases rapidly in the yellow and green, shows a very distinct minimum in the blue at about  $\lambda 508$ , and then increases towards the more refrangible end. The colour of the solution is purple. A table is given showing the absorption coefficients, for various wave-lengths, of a solution of cupric bromide in hydrobromic acid, an alcoholic solution of the anhydrous bromide, and green and blue aqueous solutions. With wave-lengths shorter than  $\lambda 660$ , the coefficient is very high.

Even when protected from light, the solutions, after a little time, contain free bromine, the quantity of which increases rapidly with an increase in the quantity of cupric bromide, but is not proportional to it, the proportions of free bromine per litre after several months being 0.880 gram, 5.120 grams, and 6.08 grams, for 0.255 gram, 0.175 gram, and 1.2 gram of copper. The hydrobromic acid is probably oxidised in presence of the cupric bromide in the same manner as hydrochloric acid in presence of certain chlorides. H. B.

**Potential of Hydrogen and some Metals.** By B. HUMANN (*Zeit. physikal. Chem.*, 14, 193—230).—Voltaic elements were formed consisting of the chain, mercury, potassium chloride, a normal salt solution, metal present in the salt. From the observations of the E.M.F., the difference of potential between the metal and its salt solution is calculable. For hydrogen salts, the electrode consisted of a platinum rod covered with a layer of platinum black, immersed in the acid and half in hydrogen. A capillary electrometer was used, and the observations lead to the following results the D.P. between the metal and solution (see next page).

It was also found that, as suspected, the last nine metals are precipitated from their solutions by hydrogen. Experiments with thallium salts indicated that, with equal concentration of the metallic ions, the negative ion has no influence on the Diff. Potential. The E.M.F.'s of chains containing various oxidisers and reducers were also

	Sulphate.	Chloride.	Nitrate.	Acetate.
Magnesium.....	+1.239	+1.231	+1.060	+1.240
Aluminium.....	1.040	1.015	0.775	—
Manganese.....	0.815	0.824	0.560	—
Zinc.....	0.524	0.503	0.473	0.522
Cadmium.....	0.162	0.174	0.122	—
Thallium.....	0.114	0.151	0.112	—
Iron (ferrous) ...	0.09	0.087	—	—
Cobalt.....	-0.0	-0.015	-0.078	-0.004
Nickel.....	0.	0.020	0.060	—
Tin.....	—	0.085	—	—
Lead.....	—	0.005	—	—
Hydrogen.....	38	0.249	—	0.150
Bismuth.....	90	0.315	0.500	—
Antimony.....	—	0.376	—	—
Arsenic.....	—	0.550	—	—
Copper.....	0.515	—	0.615	0.580
Mercury.....	0.980	—	1.028	—
Silver.....	0.974	—	1.055	0.991
Palladium.....	—	1.066	—	—
Platinum.....	—	1.140	—	—
Gold.....	—	1.356	—	—

observed, and her oxidiser (*vel. red*) gave a + difference sulphide, hydroxy

the E.M.F. between the platinum and the silver. Of the 40 compounds examined, four only of potential, namely, stannous chloride, sodium mine, and chromous acetate. L. M. J.

**The Solubility of Metals.** By H. C. JONES (*Zeit. physikal. Chem.*, 14, 346—360).—The author has determined the E.M.F. of voltaic chains in which the electrodes are silver, and the liquids are solutions of silver nitrate of equal concentration in different solvents. One solvent was in all cases water, the others being ethylic alcohol, methylic alcohol, and acetone; in all cases, the water solution was negative to the other, the E.M.F. being 0.0956 for the ethylic alcohol chain, and 0.0906 for methylic alcohol, in both cases N/10 solutions, and 0.1512 with acetone (N/100). In the case of the ethylic alcohol chain, it is possible to calculate the ratio of the tension of the metal in the two solutions, using the equation  $E.M.F. = 0.058 (\log p_1/P_1 - \log p_2/P_2)$  where  $p_1$  and  $p_2$  are the pressures of the silver ions and  $P_1$  and  $P_2$  the solution tension of silver in the two solutions, and hence results  $P_1/P_2 = 0.024$ . In other cases examined, data for the dissociation of the silver are unavailable. The observations, however, certainly indicate the tension of metals in different solvents is not constant, but is dependent on the nature of the latter. L. M. J.

**Dielectric Constants and Chemical Constitution.** By C. B. FINE (*Zeit. physikal. Chem.*, 14, 286—300).—The author determines the dielectric constant of a number of solid and liquid substances by a method dependent on the resonance of electric vibrations. Details of the method are given in the paper, and the values of  $K$  for

a large number of liquid compounds. Researches are also recorded on mixtures of water with methylic and ethylic alcohols, glycerol, and acetic acid, curves embodying the results being given. In the case of the two alcohols the curve is almost a straight line joining the values of the two compounds, but in the aqueous mixtures singular points occur at compositions corresponding with definite hydrates, for instance,  $C_2H_6O + 6H_2O$ ,  $+ 3H_2O$ ,  $+ H_2O$ ;  $CH_4O + 4H_2O$ ,  $+ 2H_2O$ ,  $+ 1\frac{1}{2}H_2O$ ;  $C_3H_8O_3 + H_2O$ ;  $C_2H_4O_2 + 2H_2O$ ,  $+ H_2O$ . The temperature variation of the dielectric constant of water was also investigated. The observed results are well reproduced by the use of the following atomic and group values, although in some cases the differences are far beyond experimental errors.

H = 2.6	OH = 1356	CH <sub>2</sub> = 41.6
O = 2.6 × 12	CO = 1520	CH <sub>3</sub> = 46.8
O = 2.6 × 16	COH = 970	S = 2.6 × 16
X = 2.6 × M <sub>x</sub>	NO <sub>2</sub> = 3090	

In the case of hydrocarbons and a large number of solids remarkable agreement is obtained by the use of the value  $K = 2.6 D$ , where  $D$  is the density of the substance. L. M. J.

**Pure Water.** By F. KOHLRAUSCH and A. HEYDWEILLER (*Zeit. physikal. Chem.*, 14, 317—330).—The electrical conductivity of water in as high a state of purity as possible was determined, and that of pure water calculated from the results. The water was distilled and examined in a vacuum, as contact with air rapidly raises the conductivity, which, in some experiments, rose from 0.11 to 0.14 in four minutes, reaching 0.58 in two hours. The results at various temperatures of the purest water obtainable were

0°.	18°.	25°.	34°.	50°.
0.014	0.040	0.058	0.089	0.176

The value  $\frac{dk}{dt}$  was calculated at various temperatures, and also the theoretical value as derived from the data of the dissociation theory, and from the result is deduced the value  $k = 0.0361$  for pure water at 18°, the difference = 0.0043 being ascribed to impurities. The values for the dissociation of water derived from these experiments then became

	0°.	2°.	10°.	18°.	26°.	34°.	42°.	50°.
$10^{10}\alpha \dots$	0.36	0.40	0.57	0.80	1.10	1.45	1.91	2.44

L. M. J.

**Electrical Conductivity of Feebly-dissociated Compounds and the Kohlrausch Method.** By M. WILDERMANN (*Zeit. physikal. Chem.*, 14, 231—246).—The author gives an account of the details of experiments on the conductivity of dichloroacetic, trichloroacetic, and  $\beta$ -resorcylic acids in absolute alcohol, all of which were carried out by Kohlrausch's method. The results of the experiments for varying dilutions are recorded, and the values for  $\mu_{\infty}/\mu_r$  compared with  $\sqrt{v_1}/\sqrt{v}$ , the law of dilution being obeyed to 18° by trichloroacetic acid. The order of the dissociation of acetic acid and its chloro-

derivatives is the same in alcohol as in water, but the resorcylic acid does not occupy the position that would be expected from its aqueous dissociation. Kohlrausch's method is, however, unsuitable for slightly dissociated compounds, and almost useless for organic bases or acids in alcohol or other organic solvent, whilst even when applicable to such cases it is extremely tedious and troublesome. L. M. J.

**A new Method for Determining the Electric Conductivity of Feebly-dissociated Compounds.** By M. WILDERMANN (*Zeit. physikal. Chem.*, 14, 247—271).—The author had previously pointed out that Kohlrausch's method is inapplicable to feebly-dissociated compounds (preceding abstract), and describes a method which, for such cases, is more satisfactory. The chief difference lies in the use of a far stronger E.M.F., by which the polarisation becomes practically negligible, and a galvanometer can be employed instead of the telephone; whilst also as the external resistances are very great, the measurement of the conductivity resolves into the measurement of the current, this being always done comparatively. The E.M.F. used was about 140—150 volts, obtained by 100 Clarke's elements, and the liquids were contained in capillary tubes of varying length and diameter. The results obtained for oxalic and acetic acids in aqueous solution are compared with those obtained by Kohlrausch's method, the agreement being entirely satisfactory. Experiments are then recorded in the case of dichloroacetic acid and trichloroacetic acid in alcoholic solution at various dilutions, and the molecular conductivity for the latter calculated, the results being  $\mu_v = 0.4294$  ( $v = 1.947$ ), and  $\mu_v = 5.343$  ( $v = 996.9$ ). It follows that trichloroacetic acid in alcohol obeys the dilution law up to 25°. L. M. J.

**Dissociation in Solution.** By A. SCHLAMP (*Zeit. physikal. Chem.*, 14, 272—285).—The degree of dissociation of a number of salts in aqueous solution was determined by the elevation of the boiling point, and from the results the value  $M/M_a$ , the ratio of the molecular weight to the apparent molecular weight in its solution. This ratio is compared with that obtained by the conductivity or other methods, and the agreement appears satisfactory, except in the case of calcium chloride. When solvents other than water are employed, however, the different methods do not give such concordant numbers, as is seen from the following table.

Salt dissolved in propyl alcohol.	$M/M_a$ from conductivity.	$M/M_a$ from boiling point.
Lithium chloride.....	1.44	1.18
Sodium iodide.....	1.34	1.04
Calcium chloride.....	1.33	—
Lithium salicylate.....	1.17	0.55
Salicylic acid.....	1.00	1.05

L. M. J.

**Colour of Salts in Solution.** By J. H. KASTLE (*Amer. Chem. J.*, 16, 326—340).—The dissociation theory alone seems incompetent to explain the following facts concerning the colour of certain salts in solution.

1. The solutions of different salts of the same metal may and do possess two or more distinct colours.

2. The colour of salt solutions, in the cold, grows lighter, or is less, on dilution.

The hydrate theory of solution also seems incapable of satisfactorily explaining the facts. For example, it is difficult to conceive how the mere addition of water of hydration should work so radical a change in the properties of a compound as to change a white substance to one which is blue or red.

In view of the fact that the two theories mentioned above do not satisfactorily account for many of the observed facts, the author advances the hypothesis that the colour of a salt solution is dependent not on the colour of the ion, but on the colour of the base or that of the acid, either or both of which may be coloured; and, further, that the base or the acid to which the colour is due may possess, according to conditions at present unknown, two or more distinct colours. The argument is largely one of analogy. It has been proven, in the case of ferric salts, that at least two soluble, colloidal modifications of the hydroxide of iron exist, one brown, the other yellow; and, whilst ferric salts, in much of their conduct, offer an extreme case, it is assumed that the differences between them and other salts are of degree rather than of kind. Hence, if two soluble hydroxides of iron have been isolated, there may be yet another of this element and two or more of any other metal whose salts are coloured.

The following facts may also be cited in support of the view that we really have the free acid and base in solutions of coloured salts.

1. Most of these salts, if not all, are acid in reaction.

2. Most of them form basic salts readily.

3. Water in many of its reactions may be regarded as an acid, and hence the formation of hydroxides in solution is similar to double decompositions.

4. The many phenomena of the coloration of salt solutions, and the changes they sometimes undergo, which, as the author shows, are accounted for by this hypothesis.

H. C.

**Solubility of Iodine in Carbon Bisulphide: Nature of Solution.** By H. ARCTOWSKI (*Zett. anorg. Chem.*, 6, 392—410; compare this vol., ii, 308).—The author has determined the solubility of iodine in carbon bisulphide at a series of temperatures lying between  $-94^{\circ}$  and  $+42^{\circ}$ ; the method used consists in saturating carbon bisulphide with iodine at the required temperature, then transferring a part of the solution to a tared flask containing mercury and again weighing. The carbon bisulphide is then evaporated off in a vacuum and the residual mercuric iodide and mercury weighed; the weight of both iodine and carbon bisulphide is thus determined. The solubility at low temperatures was determined by cooling a fairly strong solution by means of solid carbonic anhydride and ether, or some convenient cooling agent, filtering off the deposited iodine, and analysing the solution as above.

The solubility curve lying between the above limits of temperature

is composed of six straight lines connected together by short curved pieces. The author uses his results to support his previously expressed views respecting the nature of solution. W. J. P.

**Solubility of Ethylic Ether.** By J. SCHUNCKE (*Zeit. physikal. Chem.*, 14, 331—345).—The mean of a number of experiments gave the following results for the ether absorbed by 1 gram of water,

0°.....	0.12465	20°.....	0.07487
10°.....	0.09599	30°.....	0.06370

and for the water absorbed by 1 gram of ether,

10°.....	0.02702	20°.....	0.02720
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The solubility of hydrogen chloride in ethylic ether was also determined, the analyses yielding the following values for the weight of the gas in 1 gram of the solution:—

−9.2°.....	0.3751	14.8°.....	0.2780
+0.4°.....	0.35407	30°.....	0.1947

The solubility of ether in aqueous solutions of hydrogen chloride at six concentrations, varying from 3.65 to 31.61 per cent., was also determined, and the results recorded in both tabular form and by curves, a table being finally given also for the specific gravity of the acid at different temperatures. L. M. J.

**Affinity Constants of Weak Acids and the Hydrolysis of Salts.** By R. W. WOOD (*Amer. Chem. J.*, 16, 313—325).—In a preliminary paper (this vol., ii, 83) the author described a method for determining the apparent action of salts on the affinity constants of weak acids. A weighed amount of diastase is allowed to act for a given length of time, at a given temperature, on a weighed amount of starch, in the presence of known amounts of acids or salts. The action of the diastase is inhibited by acids or alkalis, and by determining the amount of sugar formed in each case the retarding power is measured. The numerical results published in the first paper are of qualitative value only, for it has since been found that slight variations in temperature, not sufficiently guarded against in the earlier work, had a far greater influence than was supposed, a change of half a degree in temperature being sometimes equivalent to a change of 10 per cent, or more, in the amount of the acid. A method of operating under conditions favourable for maintaining a constant temperature has, therefore, been devised, and is described in the paper.

The action of the fatty acids on diastase was first tried, with a view of determining the affinity constants, and comparing them with the figures obtained by other methods. Hydrochloric acid was used as a standard of comparison. The initial action of acids is, in all cases, to increase the activity of the diastase, an effect which has been noticed by Duggan and others, and is probably due to a slight

alkalinity of the starch. The following values were obtained for the affinity constant  $K$ :—

Formic acid.....	$K = 0.025$
Acetic acid.....	$K = 0.00146$
Propionic acid.....	$K = 0.0006$
Butyric acid.....	$K = 0.00071$
Isobutyric acid.....	$K = 0.0008$

These values are in the same order as those obtained by Ostwald, with the exception of the two butyric acids, which he found to have nearly the same value.

By comparing the action of the sodium salts of the fatty acids with that of sodium hydroxide, the amount of free hydroxyl, and therefore the percentage of the salt that has suffered hydrolysis, can be determined, as the salt yields free acid and free base, and the latter breaks up completely into Na and OH ions. It was found, in this way, that the percentage hydrolysed was proportional to the affinity of the acid, but no careful or extended tables were prepared.

In the presence of the salt of a weak acid, very large quantities of acid can be added without affecting the diastase, except to a very limited degree. Quantitative measurements show that this behaviour is in keeping with the dissociation theory, for, as the work of Arrhenius indicates, the presence of a salt in a solution of its acid prevents the dissociation of the latter to a degree depending on the amount of salt present.

H. C.

**Apparatus for Regulating Diminished Pressures.** By F. KRAFFT (*Ber.*, 27, 1823).—The regulator for diminished pressures, described by the author 12 years ago (*Ber.*, 15, 1693), consists of a large vessel with two taps, not of the large vessel alone, as Kahlbaum states (this vol., ii, 349).

J. B. T.

**Mechanical Agitator.** By C. MAULL (*Ber.*, 27, 1732—1733).—In this instrument, the bottle to be agitated is placed horizontally and then shaken by means of an eccentric attached to a wheel driven by a small turbine.

A. H.

## Inorganic Chemistry.

**Physical Properties of pure Nitrous Oxide.** By P. VILLARD (*Compt. rend.*, 118, 1096—1099).—Pure nitrous oxide is obtained either by preparing the hydrate, which is afterwards allowed to decompose, or by fractionating the compressed or liquefied gas. In the latter case the gas is passed through suitable absorbing and drying agents, and is then liquefied, the nitrogen that accumulates above the liquid nitrous oxide being allowed to escape from time to time. The liquid is then allowed to boil in order to expel the greater



part of the dissolved gas, is next passed into another tube, which is first washed with portions of the liquid, and is finally freed from the last traces of dissolved gas by prolonged ebullition.

The liquid thus obtained is free from less liquefiable gases, its maximum vapour pressure is independent of the volume of the vapour, and a small increase of pressure causes complete liquefaction. The densities of the gas and of the liquid at various temperatures are as follows:—

Temperature ..	0°	5°	10°	17·5°	26·5°	32·9°	34·9°	36·3°
Density of liquid	0·9105	0·885	0·856	0·804	0·720	0·640	0·605	0·572
„ gas..	0·0870	0·099	0·114	0·146	0·207	0·274	0·305	0·338

The critical temperature of pure nitrous oxide is 38·8°, a value higher than that obtained by previous observers. The critical volume is 0·00436, the critical density 0·454, and the critical pressure 77·5 atmospheres.

C. H. B.

**Volatility of Borax.** By S. WALDBOTT (*J. Amer. Chem. Soc.*, **16**, 410—418).—From the author's experiments, it is conclusively shown that borax glass is decidedly volatile at a white heat, particularly when heated in open crucibles.

Even basic borates are sensibly volatilised, which fact must not be lost from view in the analysis of borates by Rose's and Schaffgotsch's processes.

L. DE K.

**Volatility of Sodium Fluoride.** By S. WALDBOTT (*J. Amer. Chem. Soc.*, **16**, 418—420).—The author has proved by a series of experiments that sodium fluoride contained in a platinum crucible cannot be heated in the full flame of a bunsen burner without sensibly losing in weight.

L. LE K.

**Compounds of Ammonia and Silver Salts.** By JOANNIS and CROIZIER (*Compt. rend.*, **118**, 1149—1151).—When ammonia gas is passed over a metallic salt it is difficult to procure complete saturation, but if when no further development of heat takes place the tube is cooled so that the ammonia liquefies and comes into contact with the salt, complete combination takes place. The tension of dissociation of the products is given by the formula  $\log P = a/T + b \log T + c$ , in which P is the pressure in centimetres of mercury; T the absolute temperature, and a, b, and c are constants which have to be determined for each compound. The values of these constants are given for the compounds described.

Silver bromide yields three white solid compounds,  $\text{AgBr} \cdot 3\text{NH}_3$ ;  $2\text{AgBr} \cdot 3\text{NH}_3$ ; and  $\text{AgBr} \cdot \text{NH}_3$ . They dissociate under the ordinary pressure at 3·5°, 34°, and 51·5° respectively.

Silver iodide yields a white solid compound,  $\text{AgI} \cdot \text{NH}_3$ , in addition to the already known  $2\text{AgI} \cdot \text{NH}_3$ . Under the ordinary pressure they dissociate at 3·5° and 90° respectively.

Silver cyanide forms the compound  $\text{AgCN} \cdot \text{NH}_3$ , which is very soluble in liquid ammonia at -10°. Under the ordinary pressure, its

temperature of dissociation is  $102^{\circ}$ ; at  $100^{\circ}$  its dissociation pressure is 690 mm. and not 550 mm. as stated by Isambert.

Silver nitrate forms three compounds,  $\text{AgNO}_3 \cdot 3\text{NH}_3$ ;  $\text{AgNO}_3 \cdot 2\text{NH}_3$ ; and  $\text{AgNO}_3 \cdot \text{NH}_3$ . The first is very soluble in liquid ammonia below  $-10^{\circ}$ , and dissociates at  $63^{\circ}$  under normal pressure. The second compound dissociates under normal pressure at about  $170^{\circ}$ , but the phenomena are irregular.

C. H. B.

**Changes during the Remelting of Lead-tin Alloys.** By B. WIESENGRUND (*Ann. Phys. Chem.*, [2], 52, 777—792) — Rudberg (1830) observed that when alloys of lead and tin are cooled, an inserted thermometer remains stationary at two different points, the upper point varying with the composition of the alloy, the lower point being the same for all alloys, and being about  $187^{\circ}$ . The alloy of the composition  $\text{PbSn}_3$  only gives the latter point, this being the melting point of the alloy in question. These results were confirmed by Wiedemann (1878). The author has submitted these alloys to a further examination, and his results are given in the following table. In this table, the first column, I, gives the composition of the alloy under examination, II the specific gravity directly determined, III the specific gravity calculated on the assumption that no change in volume takes place on mixing the two metals, column IV contains the differences of the second and third, V the lower, and VI the higher stationary points shown by the thermometer immersed in the cooling alloy.

I.	II.	III.	IV.	V.	VI.
$\text{PbSn}_{18}$ .....	7.6660	7.8150	1490	$185.2^{\circ}$	$206.7^{\circ}$
$\text{PbSn}_8$ .....	7.9995	8.3497	3502	$184.5$	$191.0$
$\text{PbSn}_4$ .....	8.0815	8.5302	4487	$184.0$	$186.6$
$\text{PbSn}_3$ .....	8.3636	8.8524	4888	$183.0$	$183.0$
$\text{PbSn}_2$ .....	8.7298	9.1903	4605	$182.2$	$202.0$
$\text{PbSn}$ .....	9.4320	9.8770	4450	$181.3$	$242.0$
$\text{Pb}_2\text{Sn}$ .....	10.0380	10.4487	4107	$180.0$	$273.0$
$\text{Pb}_3\text{Sn}$ .....	10.3033	10.7001	3968	$178.3$	$284.0$
$\text{Pb}_4\text{Sn} + 5 \text{ grams Sn.}$	10.4122	10.7770	3645	$176.0$	$289.0$
$\text{Pb}_5\text{Sn}$ .....	10.5371	10.8414	3043	$174.3$	$295.0$
$\text{Pb}_6\text{Sn}$ .....	10.6620	10.9322	2702	$172.4$	$305.0$
$\text{Pb}_{12}\text{Sn}$ .....	11.1825	11.2493	0668	—	$317.0$

It will be seen that the maximum difference between the observed and calculated specific gravities is obtained with the alloy  $\text{PbSn}_3$ , for which the lower and higher melting points coincide. If any one of the above alloys, with the exception of  $\text{PbSn}_3$ , is remelted several times over, and the melting points again determined a slight rise is in each case found to have taken place, but in no case is a rise of more than one degree observed.

H. G.

**Stability of Dilute Solutions of Mercuric Chloride.** By L. VIGNON (*Compt. rend.*, 118, 1099—1101; compare this vol., ii, 93).—

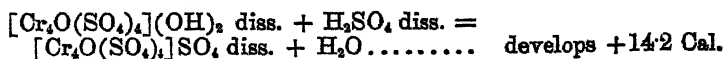
When mercuric chloride is heated at  $80^{\circ}$  for 60 hours, the residue has the composition represented by the formula  $\text{HgCl}_2$ . Repeated evaporation of a 0.1 per cent. aqueous solution in a vacuum has no effect on the solubility of the salt. A solution of this strength undergoes no change after contact with purified air for 60 days. When such a solution is partially or fully exposed to ordinary air the rate of alteration is smaller the more completely the air is excluded. (Compare Tanret, this vol. ii, 93).

When sodium hydroxide, sodium carbonate, or ammonia, are added to dilute solutions of mercuric chloride in quantity insufficient for complete precipitation, the results are irregular so far as concerns the rate of precipitation and the character of the precipitate. Sometimes precipitation is immediate, and at other times it requires several hours; sometimes the precipitate is dense and compact, and at others it is finely divided and remains in suspension. The quantity of mercury precipitated is always higher than the calculated quantity, and it increases with the time, a result which is due to the formation of oxychlorides and chloramides containing a high proportion of mercury. C. H. B.

**Production of Metallic Films specially adapted for covering Aluminium.** By C. GÖTTIG (*Ber.*, 27, 1824—1826).—Aluminium becomes covered with a hard film of copper on rubbing it with tin dipped in copper sulphate solution, the deposit increases in thickness if the coated metal is suspended in a dilute copper salt solution. Aluminium is covered with tin by rubbing it with brass moistened with solutions of certain tin salts, such as ammonium stannichloride,  $\text{SnCl}_4 \cdot 2\text{NH}_4\text{Cl}$ ; in this case, too, the deposit increases in thickness when the metal is suspended in a tin salt solution of suitable concentration. Aluminium which has been coated with copper as above described, when suspended in a solution of a tin salt, receives a coating of tin over the copper. J. B. T.

**Iron Phosphide.** By L. M. DENNIS and B. S. CUSHMAN (*J. Amer. Chem. Soc.*, 16, 477—485).—See this vol., ii, 400.

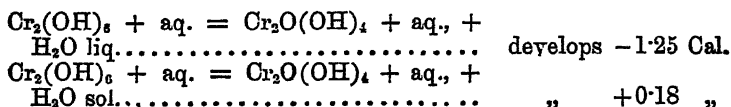
**Molecular Transformations of some Chromium Compounds.** By A. RECOURA (*Compt. rend.*, 118, 1146—1149).—The author confirms the statement of Favre and Valson, that when the green solutions of the basic sulphate  $[\text{Cr}_2\text{O}(\text{SO}_4)_4]\text{OH}$  are mixed with barium chloride in the cold, there is an immediate precipitation of one-third of the sulphuric acid only. It follows that the green solution has the composition  $[\text{Cr}_2\text{O}(\text{SO}_4)_4]\text{SO}_4 + \text{H}_2\text{SO}_4$ , the basic salt being the sulphate of the complex radicle  $[\text{Cr}_2\text{O}(\text{SO}_4)_4](\text{OH})_2$ . This base can be obtained by treating the green solution with the proper quantity of alkali; it is soluble, and its solution has a more brilliant green colour than the original solution.



When the solution of this base is mixed with a quantity of alkali

equivalent to the sulphuric acid present in the radicle, it is decomposed, and the hydrate  $\text{Cr}_2\text{O}(\text{OH})_4$  is precipitated. When this hydrate is dissolved in sulphuric acid, the latter gives normal reactions, and hence the salt  $\text{Cr}_2\text{O}(\text{SO}_4)_2$  is an ordinary basic sulphate. The green sulphate of the heated solutions, however, is not a sulphate of a hydrate  $\text{Cr}_4\text{O}(\text{OH})_{10}$ , but is the normal sulphate of *chromylhydroxide*  $[\text{Cr}_2\text{O}(\text{SO}_4)_2](\text{OH})_2$ .

By means of the action of sodium hydroxide, the author finds that



It is probable that the actual development of heat is much greater, but is masked by the heat absorbed by the preliminary separation of several molecules of water of hydration. The heat of neutralisation of the precipitated normal hydrate decreases, and tends towards the value corresponding with  $\text{Cr}_2\text{O}(\text{OH})_4$ , and the dehydration may even go beyond this point, for, after a long time, an alkaline solution of chromium hydroxide gradually deposits the oxide insoluble in dilute acids. Moreover, when precipitated chromium hydroxide is dissolved in excess of sodium hydroxide, the heat of neutralisation is lower the longer the time that has elapsed since the preparation of the solution, the value for  $2\text{H}_2\text{SO}_4$  dil. +  $\text{Cr}_2\text{O}_3$  aq. being + 25 Cal. after 10 minutes, + 22.5 Cal. after 25 minutes, and + 15.8 Cal. after 70 minutes.

C. H. B.

**Chlorochromates and Amidochromates.** By S. LÖWENTHAL (*Zeit. anorg. Chem.*, 6, 355—368).—Ammonium chlorochromate is prepared by Peligot's method by the action of chromyl chloride on an aqueous solution of ammonium chloride. It crystallises well, melts easily, is red, and dissolves in water with a crackling noise.

*Lithium chlorochromate*,  $\text{LiClCrO}_3$ , is obtained by the action of chromyl chloride on lithium chromate in aqueous solution. It crystallises in yellowish-red, lustrous crystals belonging to the monosymmetric system  $a : b : c = 1.1589 : 1 : 1$ ,  $\beta = 64^\circ 50'$ . It melts to a reddish-brown mass.

Magnesium chlorochromate is obtained by adding chromyl chloride to a concentrated solution of magnesium chloride and allowing the mixture to remain some time in a freezing mixture. It separates in reddish-yellow crystals with  $9\text{H}_2\text{O}$ . It is also obtained by adding solid chromic acid and a little acetic acid to a concentrated solution of magnesium chloride, and then cooling the mixture. When prepared by this method, it separates in red to reddish-brown crystals with  $5\text{H}_2\text{O}$ , does not give up its water of crystallisation when allowed to remain over sulphuric acid, and is very hygroscopic.

Zinc chlorochromate forms small, yellowish-red crystals with  $9\text{H}_2\text{O}$ , decomposes on recrystallisation, is very hygroscopic, and dissolves easily in water and acids. It decomposes with evolution of chlorine if left over sulphuric acid, and also when gently heated in a tube, or at the ordinary temperature in a vacuum desiccator.

The author failed to prepare the corresponding salts of barium and strontium by the method described above for magnesium chlorochromate.

Potassium amidochromate is prepared by the method described by Heintze, by passing dry ammonia into the chlorochromate. It crystallises in tablets belonging to the monosymmetric system;  $a : b : c = 1.02832 : 1 : 1.7751$ ,  $\beta = 88^\circ 3'$ .

*Ammonium amidochromate* crystallises in yellowish-red tablets belonging to the monosymmetric system,  $a : b : c = 1.0310 : 1 : 1.8243$ ,  $\beta = 85^\circ 43'$ . It dissolves easily in water with a crackling noise.

*Lithium amidochromate* crystallises in purplish-red asymmetric prisms,  $a : b : c = 0.5578 : 1 : 0.5543$ ,  $\alpha = 81^\circ 56'$ ,  $\beta = 91^\circ 0\frac{1}{2}'$ ,  $\gamma = 83^\circ 29\frac{1}{2}'$ . It is easily soluble, and melts when gently heated.

Magnesium chlorochromate, after remaining six months over calcium chloride and sulphuric acid, still contains water, and is converted into a brown mass without any evolution of chlorine or chromyl chloride taking place. On treating this dried compound with ammonia, a yellow product is obtained which contains ammonia and chlorine, and is possibly a double compound of magnesium amidochromate and magnesium chlorochromate. The author was unable to prepare zinc amidochromate.

When potassium amidochromate is mixed with concentrated solutions of acetate of magnesium, zinc, or manganese, and allowed to evaporate in a desiccator, it crystallises out unaltered. With the acetates of lead, barium, strontium, and calcium, the corresponding chromate is at once formed. With mercuric acetate, a reddish-yellow precipitate is obtained which has the composition  $\text{Hg}_2(\text{CrO}_4)_2\text{NH}_3$ . Potassium amidochromate forms double salts with magnesium sulphate, which are bright yellow, easily soluble, and crystallise extremely well.

E. C. R.

**Action of Phosphorus Pentachloride on Molybdic acid.** By E. F. SMITH and G. W. SARGENT (*Zeit. anorg. Chem.*, 6, 384—385).—When molybdic acid (1.5 grams) is heated with phosphorus pentachloride (10 grams) in an atmosphere of chlorine at  $175^\circ$ , and the product gently warmed in a current of chlorine, phosphorus oxychloride, and a compound of the composition  $\text{MoCl}_5\text{POCl}_3$ , are obtained. The latter sublimes in greenish-black crystals, and is very easily decomposed. Piutti (*Gazzetta chim.*, 9, 538), under slightly different conditions, obtained a similar compound to which he assigned the composition  $\text{MoCl}_5\text{POCl}_3$ .

E. C. R.

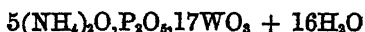
**Complex Inorganic acids. VI. Decomposition-products of Phospholutedeutungstic acids.** By F. KEHRMANN and E. BÖHM (*Zeit. anorg. Chem.*, 6, 386—391).—The authors have already shown that the yellow alkali salts of phospholutedeutungstic acid,  $3\text{RO}\cdot\text{P}_2\text{O}_5\cdot 18\text{WO}_3$ , are converted by the action of alkalis into colourless salts of the formula  $5\text{RO}\cdot\text{P}_2\text{O}_5\cdot 17\text{WO}_3$ . They have now examined this reaction quantitatively, and find that it takes place according to the equation



The luteo-salt, dissolved in a small quantity of cold water, is mixed with a cold saturated solution of potassium hydrogen carbonate until it is decolorised. After remaining a quarter of an hour, the precipitated salt is collected and dried, and the phosphoric and tungstic acids determined in the filtrate. The small quantity of phosphoric acid found in the filtrate, and the excess of tungstic acid over that required by the above equation are in the ratio 1 : 18.7, showing that the phosphoric acid is present in the form of the salt  $\text{K}_2\text{O}, \text{P}_2\text{O}_5, 17\text{WO}_3$ .

The salt  $(\text{NH}_4)_2\text{O}, \text{P}_2\text{O}_5, 17\text{WO}_3$ , when heated with excess of cold 10 per cent. hydrochloric acid and then gradually warmed to boiling as long as a white precipitate is formed, gives the following products. The white precipitate, about 4 per cent., is ammonium phosphododecitungstate,  $3(\text{NH}_4)_2\text{O}, \text{P}_2\text{O}_5, 24\text{WO}_3 + \text{aq.}$  From the filtrate, 95 per cent. of the ammonium salt of the luteo-acid is obtained by precipitation with ammonium chloride, and finally with quinoline hydrochloride. The filtrate from this second precipitation contains about 0.25 per cent. of phosphoric acid.

Analyses of the ammonium and potassium salts of the 17-series show, without doubt, that they have the composition



and  $5\text{K}_2\text{O}, \text{P}_2\text{O}_5, 17\text{WO}_3 + 21$  or  $22\text{H}_2\text{O}$ .

E. C. R.

**Chlorides of Zirconium.** By F. P. VENABLE (*J. Amer. Chem. Soc.*, 16, 469—475).—As it is very doubtful whether zirconium tetrachloride has hitherto been obtained pure, that is, free from oxychloride, the author has reinvestigated the matter. He finds that when the crystals, obtained by dissolving the oxide in strong hydrochloric acid and recrystallising from the same solvent (*Abstr.*, 1892, 412), are dried at 100—110° in a current of dry hydrogen chloride free from air, the substance first melts, and, after the loss of the moisture and excess of hydrogen chloride, resolidifies to a hard white mass which is very hygroscopic. If the drying is done very slowly, fine crystals are obtained. These crystals, giving 52.7 per cent. of  $\text{ZrO}_2$  on ignition in the air, are pure zirconium tetrachloride. This substance is very unstable, forming basic or oxy-compounds on exposure to air or moisture.

If dilute hydrochloric acid is used for dissolving the oxide, zirconium oxychloride,  $\text{ZrOCl}_2$ , is formed as a white powder insoluble in hydrochloric acid but soluble in water.

L. T. T.

**Double Bromides of Palladium.** By E. F. SMITH and D. L. WALLACE (*Zeit. anorg. Chem.*, 6, 380—383).—The double bromides are obtained by dissolving dry palladium bromide and equivalent quantities of the metallic bromide in water containing hydrogen bromide, and evaporating the mixture.

*Potassium palladium bromide*,  $\text{K}_3\text{PdBr}_4$ , crystallises in lustrous, reddish-brown needles, is anhydrous, very stable, and remains unchanged on exposure to air. When treated with bromine at 70°, with the object of obtaining the salt  $\text{K}_3\text{PdBr}_4$ , it remains unaltered, but crystallises from the solution with  $1\text{H}_2\text{O}$ . These crystals are long,

dark-brown needles, which quickly lose their lustre on exposure to air, and are converted into a reddish-brown powder.

*Ammonium palladium bromide* crystallises in beautiful olive-brown orthorhombic forms. It is anhydrous, and quite stable on exposure to air.

*Sodium palladium bromide* crystallises with difficulty in large, dark-red tablets containing 14.6 per cent.  $H_2O$ , and very easily deliquesces.

*Strontium palladium bromide*,  $SrPdBr_4 + 6H_2O$ , crystallises in short, black prisms, and is stable on exposure to air.

*Manganese palladium bromide*,  $MnPdBr_4 + 7H_2O$ , crystallises in black crystals similar in form to the ammonium salt. It is extremely soluble.

The authors were unable to obtain crystalline double haloid-salts of zinc and cadmium with palladium. E. C. R.

**Ruthenium and its Nitroso-chlorides.** By J. L. HOWE (*J. Amer. Chem. Soc.*, 16, 388—396).—Ruthenium nitroso-chloride is readily prepared by boiling the oxide  $RuO_3$  with aqua regia in a reflux apparatus, and evaporating the solution. It forms stable double salts with the alkaline chlorides; 100 parts water at  $25^\circ$  dissolve 12 parts of the potassium double salt (Joly, Abstr., 1889, 352), and 80 parts at  $60^\circ$ . Of the ammonium salt (Joly, Abstr., 1891, 401), 100 parts of water dissolve 5 parts at  $25^\circ$ , 22 parts at  $60^\circ$ . *Rubidium ruthenium nitroso-chloride*,  $2RbCl, RuCl_3 \cdot NO$ , forms a pale purple powder, which may be recrystallised from boiling water in almost black crystals resembling those of the potassium and ammonium salts. When a solution is evaporated over sulphuric acid, the *hydrated salt* crystallises with  $2H_2O$  in dark purple crystals. It loses its water on heating or over sulphuric acid. 100 parts of water dissolve 0.57 part at  $25^\circ$  and 2.13 parts at  $60^\circ$ . *Cæsium ruthenium nitroso-chloride* forms a pale purple powder or minute crystals. 100 parts of water dissolve 0.4 part at  $25^\circ$ , and 0.56 part at  $100^\circ$ . The *hydrated salt*,  $2CsCl, RuCl_3 \cdot NO + 2H_2O$ , yields large, dark purple crystals very soluble in water. 100 parts of water dissolving 105.8 parts of salt.

When the potassium salt is heated, decomposition does not commence until above  $250^\circ$ , and then the chlorine and nitroso-group are both separated together. Solutions of the nitroso-chlorides are acted on by carbamide, or reduced by ferrous sulphate, or by cuprous or stannous chlorides. Hydrogen peroxide is without action in these solutions, but when it is added to alkaline solutions oxygen is evolved and the solution decolorised. Permanganates are reduced by boiling with alkaline solutions, nitric acid being amongst the products. Sodium hypobromite causes evolution of gas, and on acidifying with hydrochloric acid ruthenium tetroxide and bromine are evolved. Potassium cyanide appears to form a double salt. Mercurous and silver salts give buff precipitates, but the other heavy metals are not precipitated.

The nitroso-chlorides may be distinguished from the trichlorides as follows. The solutions are rose-coloured, and become salmon-pink on dilution; excess of alkali does not cause a precipitate; no purple colour is given on boiling with a thiocyanate; there is no reaction with

ammonia and sodium thiosulphate; boiling a neutral solution with potassium ferrocyanide yields a very characteristic deep brown coloration.

No higher chloride than the trichloride could be obtained. The nitroso-chloride is produced by the method described by Clans for preparing his red salt, which he thought to be the tetrachloride.

The rubidium and caesium hydrated double salts were crystallographically examined by N. D. Clark. They are isomorphous, and crystallise in the monoclinic system. The axial ratios obtained were.

$2CsCl, RuCl_2 \cdot NO, 2H_2O$ ,  $a : b : c = 1.698 : 1 : 1.177$  and  $\beta = 76^\circ 11'$ .

$2RbCl, RuCl_2 \cdot NO, 2H_2O$ ,  $a : b : c = 1.692 : 1 : 1.242$  and  $\beta = 76^\circ 50.5$ .

L. T. T.

## Mineralogical Chemistry.

**Composition and Origin of Natural Gas.** By F. C. PHILLIPS (*Amer. Chem. J.*, 16, 406—429).—Continuing his researches on the phenomena of oxidation and chemical properties of gases (this vol. ii, 293, 294, and 367), the author has analysed (for method see this vol., ii, 401) a large number of natural gases from various parts of America, and one from Vancouver. These all contained from 90—99 per cent. of paraffins, and from a trace to 3.6 per cent. of carbonic anhydride, the remainder being nitrogen. A trace of hydrogen sulphide was detected in one sample, and a trace of oxygen in several, but in no case was any hydrogen or ammonia found. The absence of hydrogen was proved by passing the gas through dry palladium chloride (which is at once reduced by hydrogen), and also through solutions of palladium chloride, platinum chloride, and ammoniacal silver nitrate, when no precipitates were formed. These tests and passing through bromine water showed the absence of carbon monoxide, olefines, or members of the acetylene series. These natural gases were also not ignited by platinised asbestos below about  $300^\circ$ . Experiments specially made showed that natural gas was ignited by platinised asbestos at  $40$ — $50^\circ$  when it contained 5 per cent. hydrogen, at  $80$ — $90^\circ$  when 2.5 per cent., at  $210$ — $220^\circ$  when 0.5 per cent., and only at  $270$ — $290^\circ$  when it was free from hydrogen. The paraffins present were chiefly methane, the percentage composition, as determined by combustion, varying between  $C = 74.96$   $H = 25.04$  and  $C = 78.14$   $H = 21.86$ , though  $C = 77$  per cent. was exceeded in only two out of 17 gases.

With the aim of throwing some light on the probable origin of natural gas, 50 grams of an air-dried fucus were steeped in water and then introduced into a flask, the latter filled with water free from air and connected with a bell jar over a mercury trough. No gas appeared till the third day, when rapid evolution of gas commenced, and continued in gradually decreasing rate till the end of 10 days,



when 803 c.c. of gas had been collected, and the evolution had apparently ceased. The analysis of the gas evolved gave

	First 800 c.c.	Second 300 c.c.	Remaining 203 c.c.
Carbonic anhydride..	18.23	32.47	53.44
Methane.....	0.30	0.28	0.08
Hydrogen.....	62.24	49.97	42.02
Nitrogen.....	19.23	18.28	4.46

The apparatus was, however, still kept set up for a further two and a half years, when another 30 c.c. of gas had collected in the receiver, and this was found to consist of almost pure methane. The author considers that this extremely slow secondary decomposition of vegetable matter at about ordinary temperatures and in the absence of air must not be ignored when considering the probable sources of natural gas.  
L. T. T.

**Artificial Preparation of Hæmatite.** By H. ARCTOWSKI (*Zeit. anorg. Chem.*, 6, 377—379).—A current of ammonium chloride vapour when passed over oxide of iron, heated to dull redness, converts the oxide into crystalline hæmatite. Ferric oxide heated at 350° absorbs ammonium chloride vapour, and melts to a black mass, from which ferric chloride soon distils. The residue absorbs water from the air, and is a mixture of ammonium chloride and ferric chloride. At 600°, the ferric oxide is partially converted into small crystals, and then mechanically absorbs ammonium chloride without melting. At 700° the ferric oxide becomes crystalline. The crystals are of the same form as the hæmatite crystals from Elba. The author points out that the gases of fumaroles contain ammonium chloride, and the fissures in the vicinity are generally covered with crystals of hæmatite.  
E. C. R.

## Physiological Chemistry.

**Effects of Diminution of Oxygen on the Organism.** By T. ARAKI (*Zeit. physiol. Chem.*, 19, 422—475), and by F. HOPPE-SEYLER (*ibid.*, 476—481); compare Abstr., 1893, ii, 186, 428.—In previous communications it has been shown that diminution in the supply of oxygen to an animal will cause the occurrence in the urine of albumin, sugar, and lactic acid. Poisoning by carbonic oxide or other toxic agents produces the same result in the same way. In the present communication these observations are continued.

Certain observers have stated that sugar and lactic acid occur in the urine after severe hæmorrhages. The experiments here recorded on rabbits and dogs, in which large quantities of blood were removed, did not support this view. The urine, however, was usually albuminous.

The next series of experiments relate to the effect of diminution of oxygen supply on the alkalinity of the blood and the hepatic glycogen. The lessened supply of oxygen was produced in some cases by poisoning with carbonic oxide, in others by diminishing the amount of oxygen in the inspired air. In all cases, rabbits were used, and the result found was that the hepatic glycogen was markedly diminished, thus supporting the views of those who hold that lactic acid originates from glycogen. The alkalinity of the blood was lessened. A similar result follows the administration of amyl nitrite. The percentage of glycogen in the muscles also sinks. The quantity of urea excreted greatly diminishes during carbonic oxide poisoning. A few experiments support the statement first made by Hoffmann (*Arch. exp. Path. Pharm.*, 7, 233), that the kidneys of an animal poisoned by quinine or carbonic oxide are unable to form hippuric acid from glycocine and benzoic acid.

In another series of animals (dogs and rabbits), sodium lactate was administered. If the animals were normal, little or no lactic acid was found in the urine, which was strongly alkaline from carbonate formed from the lactate. If the animals were poisoned with carbonic oxide, the urine was strongly acid, and contained lactic acid.

Minkowski has shown that in animals from which the liver has been removed, lactic acid is formed in the urine; this can only be explained by supposing that interference with the blood circulation produces a diminished supply of oxygen.

Hoppe-Seyler's remarks are of a commendatory nature; they also include the description of an apparatus (with figure) by means of which air containing but little oxygen can be given to an animal.

W. D. H.

**Diffusion of Gases in Water.** By F. HOPPE-SEYLER (*Zeit. physiol. Chem.*, 19, 411—421; compare Duncan and Hoppe-Seyler, *Abstr.*, 1893, ii, 62, 81).—A few experiments are recorded which show the extreme slowness of diffusion of the atmospheric gases in water. This subject derives physiological importance from the consideration of the possibilities of life in marine animals at great depths.

W. D. H.

**Digestibility of Fresh Brewer's Grains and Meat Meal, Earth Nut Cake, Extracted Caraway and Fennel Seeds, Rye Bran and Dried Grains, Rice Meal, Cotton Seed Meal, Extracted Aniseed, Cocoa Nut Meal, and Poppy Cake.** By G. KÜHN and others (*Landw. Versuchs-Stat.*, 44, 1—187).—The results were obtained by direct experiments with bullocks during the years 1873—1892. The amount and composition of food and fæces, the live weight of the animals, &c., are given in tables.

N. H. M.

**Digestion of Nitrogenous Food Constituents by Treatment with Gastric Juice and Pancreas Extracts.** By G. KÜHN and others (*Landw. Versuchs-Stat.*, 44, 188—256).—Stutzer's method for determining digestibility consisted in subjecting the substance to the action of 250 c.c. of a pepsin solution (*Journ. f. Landw.*, 1880, 28, 195 and 435) for 24 hours. Experiments were instituted by the

authors to ascertain the effect, if any, of varying the amount of pepsin, the duration of the action and the amount of acid. For some foods it was found that for every two grams, 500 c c of pepsin solution, to which hydrochloric acid is gradually added to the extent of 1 per cent. (as recommended by Stutzer) should be employed, and that the action should be continued for at least 48 hours. With most foods, as the residues of fennel, anise, caraway seeds, &c., the action must be prolonged to 72, or even 84 hours. Foods not hitherto examined should be first tested in order to ascertain whether 48 hours is sufficient.

Pfeiffer (*Journ. f. Landw.*, 31, 1883, 221), in experimenting with sheep, found that they digested more nitrogenous matter than Stutzer's method indicated, and proposed the employment of pancreas solution after pepsin (*Zeit. physiol. Chem.*, 1885, 9, 211). He found that 20—30 per cent. more nitrogenous matter was digested, and that the results then approximated more closely to those obtained with live animals. Stutzer concluded that the two solvents dissolved different nitrogenous substances.

Inasmuch as it is now shown that the 24-hour treatment with pepsin solution was insufficient, and as Stutzer himself showed that a pancreas extract alone had not a greater solvent power than pepsin, it seemed possible that the action of pancreas solution on a substance already treated with pepsin might be due to the alkali employed. This is now shown to be the case by comparative experiments. With hay, linseed cake, and cotton cake, there was generally less undissolved nitrogenous matter after treatment with soda than with pancreas, and in every case both the pancreas and the soda dissolved nitrogenous matter left undissolved by pepsin. In the case of ethereal oil residues, the pancreas dissolved considerably more than the soda; this is due to the resinous matters they contain, which are first attacked by soda and then digested by the pancreas.

When the new method (more prolonged treatment with pepsin) was compared with Stutzer's method (successive treatment with pepsin and pancreas) it was found that in twelve experiments eight gave higher results (undissolved substances) with Stutzer's method, and four with Kuhn's method.

It is concluded that pepsin solutions will dissolve all the really digestible nitrogenous matter of foods, unless, as in the case of umbelliferous seeds, there is some hindrance. Treatment with pancreas is unnecessary, and the use of soda which it involves is unsafe.

The results of 22 feeding experiments with bullocks show the correctness of this view, and that the nitrogenous matter of food which is not attacked by pepsin is completely separated in the intestines. In artificial digestion, any further amount dissolved by pancreas, after treatment with pepsin, is due to the action of the soda.

The analytical results are given in tables, showing the amount of pepsin solution employed and the duration of the experiments, &c.

The experiments were made in 1882—92.

N. H. M.

**Feeding and Respiration. Experiments with Bullocks on Fat Formations from Carbohydrates, and the Relations of Food to the Elimination of Hydrocarbons.** By G. KÜHN and others (*Landw. Versuchs-Stat.*, 44, 257—582).—The object of the experiments was not so much to confirm or refute the formation of fat from carbohydrates as to obtain general knowledge as to the relation between fat formation and food. As regards the production of fat from proteids, the results of v. Voit, and v. Pettenkofer, and many others, were supposed to have established it, until Pfliiger recently (*Arch. Ges. Physiol.*, 51. 1891, 229) pointed out that v. Voit attributed too low a value for the nitrogen of flesh and too high a value for the carbon. The question of fat formation from proteids must still be considered an open one. The question of the formation of hydrocarbons is also considered, Tappeiner and others having maintained that cellulose is not digested, or only partly digested by herbivora, but that it is probably entirely transformed by micro-organisms into gaseous products of no use to the animal. The apparatus employed in the experiments is described in detail and with sketches; it consists of a respiration case, an arrangement for measuring the air passing through the case, instruments for estimating the carbon in the air, and a ventilator by means of which a constant current of air was passed through the case.

There were four series of experiments with bullocks. In series 1, the food given was hay and wheat starch; in 2, clover hay, oat straw, wheat starch, and wheat; in 3, hay and starch meal; and in 4, hay, meat-meal free from fat, and starch meal.

In considering the results, it is pointed out that a ration which maintains an animal at a constant weight does not necessarily keep it in equilibrium internally, since there is always a renewal of hair, skin, and hoof going on. Henneberg estimated a daily loss of nitrogen ( $\pm 5$  grams) and carbon (12.5 grams) from hair falling off in summer.

The results confirm the view that the amount of albumin given in food controls the decomposition, but not the deposition of albumin, and that any increase of food over the smallest quantity required gives rise to a production of fat; it is immaterial whether the excess of food is nitrogenous or non-nitrogenous. Bullocks fed with 31.04 kilos. of digestible organic matter with a nutritive ratio of 1:4.5—7.2 deposited 2.049 kilos. of fat, whilst bullocks with 30.52 kilos. of digestible food with a nutritive ratio of 1:14.0—17.4 deposited 2.138 kilos. of fat. A given amount of gluten may thus be replaced by a similar amount of starch without affecting the amount of fat formed. Within certain limits, fat production progresses approximately with the excess of food given. This is shown by the following average results:—

	Organic matter digested.	Fat deposited.
Means of Expt. 1—5....	9.10 kilos.	0.446 kilo.
„ 6—10....	9.73 „	0.640 „
„ 11—14....	10.78 „	0.852 „

For every kilogram of starch meal in excess of food actually  
31—2

required there will be a deposition of about 0.2 kilo. of fat: how much of this fat is formed directly from starch and how much (through the saving effect of starch) from the fat of the food, and from decomposed albumin remains undecided. The experiments show conclusively that fat is formed from starch meal.

As regards the production of hydrocarbons, there was always a certain amount of gaseous hydrocarbon, but not in anything like the quantity to be expected according to Tappeiner's results. Nitrogenous food does not seem to produce hydrocarbons to any extent, if at all, but starch and other non-nitrogenous foods seem to give rise to their formation to about the same extent as cellulose; so that cellulose is practically as nutritive as starch, and the so-called non-nitrogenous extracts, and there is no reason at all why its nutritive value should be called in question. The conditions of the experiments made it impossible to ascertain whether fat when undergoing change in the intestines yields any hydrocarbon. N. H. M.

**Putrefaction of Proteid in the Intestine.** By K. SCHMITZ (*Zeit. physiol. Chem.*, 19, 378—400; 401—410).—The first paper relates to the influence of milk, kephir, and cheese on intestinal putrefaction. That milk exerts an anti-putrefactive influence is well known, although observers differ as to the constituent to which milk owes this property. The criterion of the amount of putrefaction taken is the quantity of ethereal hydrogen sulphates in the urine. Judged by this standard, cheese lessens putrefaction. This effect, however, is not produced by casein, and the lactose is held to be the responsible agent in cheese as well as in milk and kephir.

The second paper relates to the influence of hydrochloric acid on putrefactive processes. Administration of the acid in dogs produced no result; but in men it lessened the output of ethereal hydrogen sulphates. This difference of action in the two animals is considered to be due to the fact that the acid in the gastric juice of the dog is already present in sufficient quantity to produce a maximum effect.

W. D. H.

**Fats of Human Milk.** By E. LAVES (*Zeit. physiol. Chem.*, 19, 369—377; compare Ruppel, this vol., ii, 326).—The fat of human milk is very poor in volatile acids and acids soluble in water, but rich in unsaturated acids. The fat contained

1.4	per cent.	of volatile acids.
1.9	„	acids soluble in water.
49.4	„	unsaturated acids.

The volatile acids contain about equal quantities of caproic, caprylic, and capric acid, and the merest traces of butyric acid. The acids mainly present are palmitic, stearic, and oleic acids (as is usual in animal fats), and one or more acids of lower molecular weight, probably myristic acid. The melting point of these fatty acids lies between 37° and 39°, of the fat itself 30—31°. There are therefore important differences in the fats of cow's milk and of human milk.

W. D. H.

**Carbohydrates of Normal Urine.** By K. BAISCH (*Zeit. physiol. Chem.*, 19, 339—368; compare Abstr., 1893, ii, 542).—The two carbohydrates in normal urine, identified by a very complete examination of their reactions and properties, are glucose and a dextrin-like substance (animal gum). The quantity of glucose averages 0.005 per cent., and of total carbohydrate reckoned as glucose about twice that amount.

There appears also to be a small quantity of a third reducing carbohydrate, which was not, however, satisfactorily identified.

W. H. D.

**Sarcolactic acid in Pathological Urines.** By E. SCHÜTZ (*Zeit. physiol. Chem.*, 19, 482—487).—The detection of small quantities of sarcolactic acid added to the urine is quite feasible. The method employed is described.

Morbid urines from 30 patients suffering from a variety of diseases, some of which previous observers have stated lead to the excretion of sarcolactic acid, were examined always with negative results.

A crystalline compound of zinc was, however, obtained, which might be mistaken for zinc sarcolactate; but analysis showed it could not be such; moreover, it contained nitrogen. The chief substance present in the crystals is considered to be zinc hydroxyphenylacetate, or a mixture of this with zinc hydroxyphenylpropionate; perhaps hippuric acid is present also.

W. D. H.

**Action of definitely-related Chemical Compounds on Animals.** By W. GIBBS and E. T. REICHERT (*Amer. Chem. J.*, 16, 443—449; compare Abstr., 1890, 280, 813, 1018; and 1891, 1280 and 1393).—Being obliged to abandon this investigation, the authors propose, in this and succeeding papers, to recapitulate and summarise the results they have obtained.

Starting from phenol, the authors find that the substitution of hydroxyl for hydrogen atoms does not materially change, but intensifies, the physiological action, although position-isomerism exerts also a marked influence on intensity and sometimes even on the character of the action. With the phenols, those having the greatest reducing action have generally the greatest physiological action. The substitution of alkyl-radicles for hydrogen changes the mode of physiological action. The substitution of the nitro-group for hydrogen tends both to change and intensify physiological action. With mononitrophenols, the action is mainly on the circulation, and hardly at all on the nervous system, and increases from the ortho- to the para-compound. Further substitution of nitro-groups increases the intensity of action. The nitrobenzenes are somewhat similar in action to the nitrophenols, but less powerful. The nitranilines all stimulate the peripheral ends of the vagi and alter the hæmoglobin of the blood, but have little action on the nervous system, so that, in this case, the action of aniline (mainly nervous) is completely changed by the introduction of the nitro-group. In the toluidines, the result of the introduction of methyl in the aniline is somewhat similar to that of the nitro-group, reducing very much the action on the nervous system, and much increasing that on the vascular system.

L. T. T.

**Physiological Action of Hydrazine and Dibenzoyldiamide.** By P. BORISSOW (*Zeit. physiol. Chem.*, 19, 499—510).—Curtius showed that hydrazine unites firmly with aldehyde groups. Hence it is important to investigate its action on the organism. Loew (Abstr., 1891, 239) has shown that it rapidly kills seedlings, fungi, and infusoria. In the present experiments, it was subcutaneously injected in dogs. In small doses (0.05 gram of the hydrazine sulphate per kilo. of body weight) it produced slight stimulation; in large doses (0.1 gram per kilo.) the stage of stimulation was more intense, and followed by depression, ending in coma and death in two days. Given by the mouth, it produced salivation and sickness. The heart went more quickly at first, then slowed gradually and became irregular. The respiratory movements reminded one of asthma. The temperature of the body sinks.

The urine was strongly acid, and contained small quantities of the unchanged hydrazine, a small amount of albumin, in one case bile pigment, and in most cases considerable quantities of allantoin. The saliva, which is abundant, also contained allantoin.

At the autopsy, the most marked sign found was hyperæmia of the intestine, liver and kidneys.

Three experiments were made with bibenzoylhydrazine; its toxic effect is about five times weaker than that of hydrazine. The symptoms differ somewhat from those produced by hydrazine. In one experiment, allantoin was found in the urine. The cause of the excretion of allantoin is considered to be disordered metabolism produced in the liver, so that uric acid is not formed there normally.

W. D. H.

**Physiological action of the Compounds of the Cocaine Series.** By P. EHRLICH and A. EINHORN (*Ber.*, 27, 1870—1873).—Cocaine, in addition to its action as an anæsthetic, produces a very marked change in the liver, which is characterised by a great increase in the volume of that organ and a specific degeneration of the liver cells (Ehrlich, *Deut. med. Woch.*, 1890, No. 32). This property is not possessed by ecgonine, its ethers or benzoylecgonine, whereas the ethers of benzoylecgonine (Falck, *Inaugural-Diss. Kiel*, 1886) and the ethers of derivatives of ecgonine containing other acid radicles, such as isatropyl, cinnamyl, phthalyl, phenylacetyl, &c., act on the liver in the same way as cocaine itself. Of all these compounds, only the phenylacetic derivative is an anæsthetic, and the same relations hold for the *d*-cocaines.

Orthochloro- and metanitro-derivatives of both *l*- and *d*-cocaine have but little anæsthetic action but produce the characteristic effect on the liver, whilst the metamido-compounds are devoid of both these properties. The metahydroxy-derivatives occupy an intermediate position, having a very slight anæsthetic action, and only producing the characteristic action on the liver in large doses. When the acetyl- or benzoyl-group is introduced into the amido-group of the amido-cocaines, the substances obtained act on the liver but are not anæsthetics, whilst the cocaine-urethanes are much more powerful anæsthetics than cocaine itself, and also have the characteristic action on the

liver. On the other hand, metabenzenesulphamido-*d*-cocaine and *d*-cocainecarbamide have no anæsthetic effect, so that this property does not simply depend on the neutralisation of the basic amido-group by an acid radicle. The colouring matters derived from *d*-cocaine have also been examined; *d*-cocaineazodimethylaniline hydrochloride only produces extremely slight anæsthesia, whereas *d*-cocaineazo- $\alpha$ -naphthylamine hydrochloride is an anæsthetic, but does not act on the liver. The norcocaines have a more powerful anæsthetic action than the cocaines themselves, and also act on the liver, but they are much more violent poisons.

The compounds of cocaine with methylic iodide possess none of the characteristic physiological properties of the cocaines.

The power of producing anæsthesia is by no means confined to the alkaloids of the cocaine series, since it is common to many benzoyl and other derivatives of alkaloids, which will form the subject of further communications.

A. H.

## Chemistry of Vegetable Physiology and Agriculture.

**Composition of Yeast.** By P. GUICHARD (*Bull. Soc. Chim.*, [3], 11, 230—239).—See this vol., ii, 395.

**Constituents of the Nodes and Internodes of the Sugar Cane.** By J. L. BEESON (*Amer. Chem. J.*, 16, 457—464).—It being a belief among sugar planters that the nodes (joints) of the sugar cane are the main source of the reducing sugars contained in the expressed juice, the author has investigated the subject. The nodes and internodes of *a*, ripe growing canes, *b*, dead canes in varying stages of decay, and *c*, canes where the node-eyes were in different stages of development or germination were examined. The results obtained were as follows. The juice expressed from the nodes of the cane is quite different from that of the internodes. That from the nodes is highly coloured, gives a heavy precipitate with basic lead acetate, and a heavy coagulum on boiling; that from the internodes is clear, light in colour, gives only a small precipitate with lead acetate, and no appreciable coagulum on boiling. The juice from the nodes contains markedly less (in ripe growing canes from about one-half to one-tenth) reducing sugars, more solids not sugars, and more coagulable substances. The fibre of the nodes contains more proteids, and more insoluble carbohydrates not sugars, which readily pass into reducing sugars. As the cane deteriorates (decays), reducing sugars are formed more rapidly in the nodes than in the internodes, and probably glucose is the first visible product of plant assimilation by the young cane. The author believes that these facts can be best explained by the hypothesis that the physiological function of the node in the cane is similar to that of the seeds in flowering plants, namely, to store food in the region of the germinating eye for the



use of the young plant before it has taken sufficient hold of the earth to draw sustenance from the atmosphere and soil. This hypothesis is confirmed by the fact that the isolated nodes of the sugar cane when planted will germinate and grow to maturity. If this hypothesis is correct in the case of the cane, it may be true also in the case of other plants which propagate from the nodes. L. T. T.

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## Analytical Chemistry.

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**Detection of Hydrochloric acid.** By A. VILLIERS and M. FATOLLE (*Compt. rend.*, 118, 1152—1154, and 1204—1206).—The method is based on the fact that, with an acid solution of aniline, iodine produces no apparent reaction, or yields a colourless, soluble, substitution derivative, bromine forms a white, insoluble, substitution derivative, whilst chlorine forms products which are black, and insoluble with a large proportion of the gas, and with a small proportion are violet-red when warm, and blue when cold, gradually changing to red.

The aniline solution whilst acid must not contain a large quantity of an inorganic acid. The following solution answers well, and can be kept unchanged for a long time in yellow glass flasks; colourless saturated aqueous solution of aniline, 400 c.c.; glacial acetic acid, 100 c.c.

The liquid, previously concentrated or diluted to 10 c.c., is placed in a small flask, and 5 c.c. of a mixture of equal volumes of sulphuric acid and water is added, and then 10 c.c. of a saturated solution of potassium permanganate. The flask is gently heated, and the gas evolved is passed into 3—5 c.c. of the aniline solution contained in a tube surrounded by cold water. The reaction will detect 0.001 gram, or even 0.0005 gram, of hydrochloric acid when mixed with 1000 parts of bromine or iodine, but the presence of a considerable quantity of bromine reduces the delicacy of the reaction, in consequence of the formation of bromine chloride.

In presence of bromine, the halogens are precipitated in the form of silver salts, and the precipitate is digested for some time with a mixture of 10 vols. of water and 1 vol. of ammonia solution. Silver iodide is not dissolved at all, silver bromide is dissolved only very slightly, whilst the silver chloride is dissolved more or less completely. The reduction of the filtered liquid by means of zinc or magnesium and an acid, does not give very satisfactory results, and it is best to expel the ammonia *completely* by boiling, and then add hydrogen sulphide. The filtrate is afterwards boiled and concentrated to 10 c.c.

Ordinary corks should not be used in the construction of the apparatus, and the oxidation should take place in a flask provided with a glass stopper, and with a delivery tube attached by fusion.

When cyanides are present, cyanogen chloride may be formed, but hydrocyanic acid is easily expelled by heating with dilute sulphuric acid. In the case of complex cyanides, the liquid must first be distilled with sulphuric acid until vapours of the latter begin to pass over, mixed with water, and again distilled, the two distillates being afterwards mixed, and concentrated by evaporation.

When the halogens are not precipitated as silver salts, ammonium salts, if present, may interfere, in consequence of their well known reaction with chlorine. Ammonium compounds can, however, easily be expelled.

C. H. B.

**Estimation of Sulphur in Pyrites.** By T. S. GLADDING (*J. Amer. Chem. Soc.*, 16, 398—404).—The author recommends the following process. 1 gram of the finely powdered and dried ore is introduced into a beaker and mixed with 10 c.c. of bromine solution (50 c.c. bromine, 78 grams potassium bromide, in 500 c.c. of water), and allowed to remain 10 minutes in the cold, when 10 c.c. of nitric acid is added. The beaker, which must have a glass cover on it, is put into a water-bath, which is then slowly heated to boiling; when solution is effected, the liquid is evaporated to dryness. The contents are moistened with 10 c.c. of hydrochloric acid, the cover is once more put on, and when violent action has ceased, the whole is evaporated to dryness once more; the residue is now moistened with 1 c.c. of hydrochloric acid, and then digested with 50 c.c. of hot water until completely dissolved. The filtrate is precipitated hot, with a slight excess of ammonia, the precipitated ferric hydroxide is washed six times with hot water, and the filtrate, after adding a slight excess of hydrochloric acid, is precipitated, while boiling, with barium chloride solution (10 per cent.).

The ferric hydroxide may retain a trace of sulphuric acid, but this may be recovered by dissolving it in dilute hydrochloric acid and precipitating with barium chloride. One filter will do for the two precipitates.

L. DE K.

**Colorimetric Estimation of Ammonia.** By L. ILOSVAY DE NAGY ILOSYA (*Bull. Soc. Chim.*, [3], 11, 216—226).—The author recommends the employment of Wolff's colorimeter for the estimation of small quantities of ammonia. Frommendorff's method is the best for the colorimetric determination of nitrous acid; the estimation of nitric and nitrous acids by reduction to ammonia by distillation with metallic iron, is only accurate if the iron is pure. Full directions for carrying out the various operations are given.

W. J. P.

**A Wet Method for Estimating Nitrogen in Nitrates and in Nitro- and Nitroso-Compounds.** By M. KRÜGER (*Ber.*, 27, 1633—1635).—0.2—0.3 gram of the substance to be analysed is mixed with 20 c.c. of water (or of alcohol, if it is insoluble in water), 10 c.c. of a strongly acid solution of stannous chloride in hydrochloric acid, and 1.5 gram of tin, best obtained by precipitating a solution of stannous chloride with zinc. The mixture is heated with a small flame until all colour has disappeared and the tin is entirely dissolved. It

is then cooled (or the alcohol, if any was used, is evaporated), treated with 20 c.c. of strong sulphuric acid, and heated until copious fumes of sulphuric acid are evolved. In the case of a nitrate, it is now only necessary to make the solution alkaline and distil off the ammonia. In the case of a nitro- or nitroso-compound, an amido-derivative will now be present, and this must first be oxidised as described in this vol., ii, 258 (where 0.2—0.8 is a misprint for 0.2—0.3 gram). The results are accurate. If the substance is volatile with steam in acid solution, it must be heated very gently on the water bath with the tin and stannous chloride until the reduction is complete. It is even better to carry out the reduction in a sealed tube at 100°.

C. F. B.

#### Estimation of very small Quantities of the Nitrogen acids.

By G. LUNGE and A. LWOFF (*Zeit. angew. Chem.*, 1894, 345—350).—

*Estimation of Nitric acid.*—This may be accurately effected by a colorimetric test. 0.2 of brucine is dissolved in 100 c.c. of pure sulphuric acid. 0.0721 gram of potassium nitrate is dissolved in 100 c.c. of water and 10 c.c. of this is diluted to 100 c.c. with strong sulphuric acid. 1 c.c. of the nitrate solution to be tested is mixed with 1 c.c. of the brucine solution and diluted with sulphuric acid to 50 c.c.; a red colour makes its appearance, but cannot be taken advantage of. The contents are temporarily put into a beaker and heated to 70—80°, which will change the colour to a permanent greenish-yellow. Trial experiments are now made with the standard nitrate solution, until the same tint is obtained, when the operation is finished. Contrary to general belief, the reaction is not interfered with by the presence of a nitrite.

*Estimation of Nitrous acid in Commercial Sulphuric acid.*—1 c.c. of Griess's reagent is put into each of a pair of Nesslerizing tubes and mixed with 40 c.c. of water and 5 grams of sodium acetate. To the contents of the first tube 1 c.c. of the suspected acid is added and to the other, without delay, 1 c.c. of a standard nitrite solution, prepared by dissolving 0.0493 gram of pure sodium nitrite in 100 c.c. of water and diluting 10 c.c. of this to 100 c.c. with pure sulphuric acid. The reddish colours may be compared after any convenient time, but it is best to wait five minutes.

The authors prepare Griess's reagent as follows:—0.1 gram of white  $\alpha$  naphthylamine is boiled for 15 minutes with 100 c.c. of water and mixed with 5 c.c. of glacial acetic acid. The solution is then mixed with 1 gram of sulphanilic acid dissolved in 100 c.c. of water, and the mixture preserved in a well corked bottle. If, in course of time, it should become rather too red, it may be decolorised by shaking it with zinc dust.

L. DE K.

*Estimation of Phosphoric acid.* By S. W. JOHNSON (*J. Amer. Chem. Soc.*, 16, 462—465).—The author states that although the citrate method generally gives good results, this is only caused by a fortunate compensation of errors, the magnesia precipitate being contaminated with lime and also with iron and alumina, whilst the filtrate retains notable quantities of phosphoric acid.

As regards the molybdate precipitation, the process generally gives

results which are too high, and if an effort be made to prevent this by adding more nitric acid the results will be too low, unless the filtrate is further digested with more molybdate solution. L. DE K.

**Estimation of Silica in Blast Furnace Slag.** By P. W. SHIMER (*J. Amer. Chem. Soc.*, 16, 501—502).—The author points out that spinel is not decomposed by the usual alkali carbonate fusion, and remains in consequence with the silica. It is, therefore, never safe to omit the treatment of the weighed silica with sulphuric and hydrofluoric acids to ascertain its purity.

Spinel may be detected by repeatedly boiling slag with hydrochloric and hydrofluoric acids, followed up by boiling with sodium carbonate. It is then left behind as a crystalline powder. L. DE K.

**Sources of Error in Potash Estimations.** By N. ROBINSON (*J. Amer. Chem. Soc.*, 16, 364—372).—The determination of potash in commercial potash salts or fertilisers is, as yet, in a somewhat unsatisfactory state. The author points out a few sources of error. In the Lindo-Gladding process, for instance, error is introduced by the action of the solution of ammonium chloride on the precipitated potassium platinochloride, a slight double decomposition taking place, some potassium going into solution and a corresponding amount of ammonium passing into the precipitate.

In the Stassfurt or German method of analysis, the sulphates which are present are decomposed by means of barium chloride; the author calls attention to the large amount of potassium which is carried down, by occlusion, as he calls it, by the barium sulphate, and is not completely removed by washing. L. DE K.

**Electrolytic Analyses.** By F. RÜDORFF (*Zeit. angew. Chem.*, 1894, 388—389).—The present paper (compare *Abstr.*, 1893, ii, 305, 391) deals mainly with the separation of mercury from other metals.

**Mercury from Cadmium.**—The liquid is mixed with 2 c.c. of nitric acid (sp. gr. 1.2) and diluted to 120 c.c. It is then electrolysed with two Meidinger cells. If the cadmium largely preponderates, 5 c.c. of acid is added. After about eight hours, the mercury will have completely separated.

**Mercury from Zinc.**—The metals may be in the form of chlorides or nitrates. The neutral solution is mixed with 1 c.c. of nitric or 10 drops of sulphuric acid, diluted to 120 c.c., and electrolysed with two or three cells. If four cells be used, some zinc is also deposited.

**Mercury from Iron.**—The liquid is mixed with 4—5 drops of sulphuric acid, diluted to 120 c.c., and electrolysed with two or three cells.

**Mercury from Nickel.**—The liquid is mixed with 6 drops of sulphuric acid, diluted to 120 c.c., and electrolysed with two or three cells. The mercury is completely precipitated in the course of a night.

**Mercury from Manganese.**—The liquid is mixed with 3 drops of 10 per cent. sulphuric acid, diluted to 120 c.c., and electrolysed with two cells. The amount of manganese should not exceed 0.03 gram, otherwise it will not firmly adhere to the + electrode. It separates as hydrated manganese dioxide. L. DE K.

**Valuation of Zinc Dust.** By O. BACH (*Zeit. angew. Chem.*, 1894, 291—292).—1 gram of the sample is placed in a flask containing a little water and a small cylinder filled with a sufficiency of sulphuric acid; the flask is fitted with a doubly perforated india-rubber cork, through which pass two glass tubes bent at right angles, one of which reaches nearly to the bottom of the flask, and is in connection with a carbonic anhydride apparatus, whilst the other is connected with a delivery tube leading to a burette filled with, and standing over, 10 per cent. aqueous soda. Carbonic anhydride is first passed until all the air has been expelled, and, after connecting the delivery tube with the burette, the sulphuric acid is made to run into the flask. After the action has ceased, more carbonic anhydride is passed, until the volume of gas in the burette no longer increases; the burette is transferred to a large cylinder filled with water, and, after levelling, the volume of hydrogen is read off and corrected for temperature and pressure. The calculation may be avoided by using Dietrich's tables.

L. DE K.

**Analyses of Zinc, Zinc Dust, Zinc Ores, &c.** By F. MEYER (*Zeit. angew. Chem.*, 1894, 391—395).—*Estimation of Zinc in Ores.*—0.5 gram of the dry, powdered sample is treated as usual with 10 c.c. of nitrohydrochloric acid, and after the excess of acid has been expelled by heat, the residue is taken up with 10 c.c. of bihydrated sulphuric acid and heated until sulphuric fumes appear, so as to separate the lead. When cold, the mass is dissolved in 60—80 c.c. of hot water, and boiled with 10 c.c. of solution of sodium thiosulphate (1—8) to precipitate any copper, cadmium, &c.; after filtering, any iron is oxidised by adding 5 c.c. of nitric acid, and the liquid is boiled to better separate the sulphur. Iron and alumina are now precipitated by the addition of 30 c.c. of ammonia, and, when cold, 20 c.c. of bromine water is added to remove any manganese. The precipitate is collected, redissolved in acid, and reprecipitated with ammonia and bromine water to free it from zinc; the united filtrates are then made up to 500 c.c., and an aliquot part titrated with sodium sulphide (Schaffner's process).

The process is also applicable to the analysis of spelter, zinc fume, zinc dust, and zinc white. Sulphur is best estimated by Lunge's process (oxidation by nitric acid and potassium chlorate, removal of iron by ammonia, and precipitation of the sulphuric acid by barium chloride).

L. DE K.

**Analytical Properties of Iron Phosphide and Phosphate.** By L. M. DENNIS and B. S. CUSHMAN (*J. Amer. Chem. Soc.*, 16, 477—485).—The authors prepared iron phosphide by decomposing ferrous chloride at a red heat by hydrogen phosphide. Contrary to expectation, the product gave analytical results corresponding with the formula  $\text{FeP}$ , and not  $\text{Fe}_3\text{P}_4$ . It has been proposed to effect the separation of iron phosphide from iron phosphate by means of a current of chlorine at a white heat, but, although this method behaves admirably for the simple substances, the authors found it quite

unsuited for an analysis of a mixture. Other methods of analysis were also found to be unsatisfactory. L. DE K.

**Estimation of Nickel by means of Mercuric Ammonium Cyanide.** By F. W. SCHMIDT (*Ber.*, 27, 1624—1627; compare this vol., ii, 160).—The solution of nickel salt is mixed with ammonium nitrate in excess, and ammonia added until the liquid is coloured pale blue; it is then boiled, and the nickel precipitated with hydrogen sulphide solution in excess. The nickel sulphide may readily be collected on a filter, and is as stable in air as cupric sulphide. After washing with hydrogen sulphide solution, it is converted into oxide by the action of mercuric ammonium cyanide, in the manner previously described (*loc. cit.*). The results of determinations given in the paper, made by the author and others, agree closely with the theoretical. The action of ammonium nitrate in facilitating the precipitation of nickel sulphide is not unique, but is analogous to the action of other neutral salts, such as sodium chloride, potassium iodide, magnesium sulphate, &c., on the yellow solution of oxythio-arsenious acid, or on the orange-red solution of thio- or oxythio-antimonious acid; these appear to be colloidal solutions, which the neutral salts coagulate. The author's previous suggestion (*loc. cit.*), that mercuric ammonium cyanide would be found to decompose natural sulphides, is confirmed, so far as regards copper pyrites, which is quickly converted into a mixture of ferric and cupric oxides; the same result is attained by carefully roasting the finely-divided mineral in a porcelain crucible. J. B. T.

**Separation of Titanium from Iron.** By C. BASKERVILLE (*J. Amer. Chem. Soc.*, 16, 427—428).—The separation of titanium from iron, by means of sulphurous acid, has been confined to their sulphates. The process is tedious, and often unsatisfactory.

The author has, however, found that the separation is rendered easy and accurate when the chlorides are acted on. Sulphates may be changed into chlorides by precipitating with ammonia and redissolving in hydrochloric acid, the excess of which is then again neutralised. L. DE K.

**Estimation of Zirconium by means of Sulphurous acid.** By C. BASKERVILLE (*J. Amer. Chem. Soc.*, 16, 475—476).—The author has found that zirconium may be accurately estimated, and even quantitatively separated from iron and aluminium by boiling with sulphurous acid, but the reaction only succeeds when the metals exist as neutral chlorides. If, as usually happens, the salts exist as acid sulphates, these must be first converted into chlorides by precipitating with ammonia and carefully redissolving in hydrochloric acid. Iron is titrated in the filtrate from the zirconium. The test-analyses prove the great accuracy of the process. L. DE K.

**Quantitative Analysis of Natural Gas.** By F. C. PHILLIPS (*Amer. Chem. J.*, 16, 412—416).—As in natural gases higher members of the paraffin series than methane may be present, the Bunsen

method of analysis is difficult, if not impossible. The author, in his work (this vol., ii, 387), has substituted with advantage combustion of the gases over copper oxide. After determining the carbonic anhydride, olefines, &c., in the usual way, a given volume of the residual gas is slowly passed from a graduated and specially arranged pipette, over red-hot copper oxide in a combustion tube, and the water and carbonic anhydride formed, are absorbed, and weighed in the usual way. Before combustion, the tube is washed out with pure nitrogen, and afterwards, first with nitrogen, and finally with air. The nitrogen is determined by a modification of the usual volumetric combustion method. In this way the volume of the paraffin and the weights and ratio of the contained carbon and hydrogen are determined. This gives some indication of the composition of the gaseous paraffins present, and valuable data are obtained for determining the heating value of the gas.

L. T. T.

**The Iodine-Absorption of some of the Rarer Fatty Oils.** By J. A. ROELOFSEN (*Amer. Chem. J.*, 16, 467—469).—The iodine absorption figures for about 50 vegetable and animal oils (mostly rare, and previously undetermined) from trustworthy sources, were determined by the Hübl method, as described in Allen's "Commercial analysis," and the results and descriptions of the oils are given in the paper.

L. T. T.

**Estimation of Rosin Oil in Mineral Oils.** By P. C. McILHINEY (*J. Amer. Chem. Soc.*, 16, 385—388).—After describing various published processes for effecting the separation, the author finally recommends the following method. 50 c.c. of nitric acid of 1.2 sp. gr. is heated to boiling in a 700 c.c. flask, and after removing the source of heat 5 grams of the suspected oil is added. The flask is then heated on the water-bath, with frequent shaking, for about 20 minutes, when about 400 c.c. of cold water is added. After cooling, the liquid is shaken with 50 c.c. of light petroleum, which dissolves the oil which has not been acted on. The liquid is now carefully poured off from the resinous matter into a separator, and, after settling, the aqueous portion is drawn off, and the petroleum poured into a tared flask. The flask containing the resin is rinsed out with some more light petroleum which is then also introduced in the tared flask. After distilling off the solvent, the oil is weighed. It must be remembered that even pure mineral oils lose about 10 per cent. of their weight by the nitric acid treatment. The test-analysis is very satisfactory.

L. DE K.

**Estimation of Lecithin in Plants.** By B. v. BITTO (*Zeit. physiol. Chem.*, 19, 488—498).—If any vegetable tissue is extracted first with ether, and then twice with alcohol, each extraction lasting an hour, only a part of the lecithin goes into solution. It is necessary, after extraction with ether, to extract with boiling ethylic alcohol 30, or with methylic alcohol 20 times at least. Each extraction should last 8—10 minutes, never longer than a quarter of an hour.

W. D. H.

**Alkaloid-like Reactions of Acetanilide.** By E. SCHÄR (*Arch. Pharm.*, 232, 249—261).—Many of the colour reactions of acetanilide are similar to those of the common alkaloids; the author has made a comparative study of these, and tabulates his results for analytical purposes.  
W. J. P.

**Estimation of Cystin.** By P. BORISSOW (*Zeit. physiol. Chem.*, 19, 511—520).—Breuzinger showed that cystin hydrochloride formed with mercuric chloride an almost insoluble crystalline compound. In the present research some experiments are recorded in which an attempt was made to estimate cystin in a similar way. In aqueous solutions, fairly good results were obtained, if a number of precautions are observed, which are fully described. In urine, however, the difficulties do not appear to have been satisfactorily overcome; the experiments made are described in full.  
W. D. H.

**Estimation of Nicotine in Tobacco.** By G. HEUT (*Arch. Pharm.*, 231, 658—663).—Having reviewed the methods which have been suggested for the estimation of nicotine in tobacco (*Abstr.*, 1892, 771; 1893, ii, 504), the author concludes that Kissling's method (compare Vedrodi) is the most generally applicable. By adopting Pezzolata's method for separating nicotine and ammonia (*Abstr.*, 1893, ii, 504), he has proved that when anhydrous ether is employed in Kissling's method, a distillate which is free from ammonia is obtained.

Pezzolata's suggestion that magnesia should be used as the base for the liberation of the nicotine was found to be valueless in the author's hands. It is pointed out that not only does ammonium sulphate partially dissociate during the evaporation in Pezzolata's method, but also the nicotine sulphate. Acid nicotine sulphate is, however, free from this fault, so that care must be taken that the base is converted into the acid salt.  
A. G. B.

**Rapid Titration of Xantho-uric Compounds in Urine.** By G. DENIGÈS (*Bull. Soc. Chim.*, [3], 11, 226—230).—The xantho-uric compounds (uric acid, xanthine, &c.) in urine are usually determined by Haycraft's method, which consists in adding ammoniacal silver nitrate and sodium hydrogen carbonate or a magnesium salt, and determining the amount of silver in the precipitate. The complete filtration of the silver salt is, however, a very long process; the author therefore determines the silver remaining in an aliquot part of the filtrate, and thence deduces the amount of silver precipitated.

A solution (A) is made by dissolving 150 grams of ammonium chloride and 100 grams of magnesium chloride per litre in strong ammonia, and mixing the resulting solution with an equal volume of decinormal silver nitrate solution. Another solution (B) contains 10 grams of pure potassium cyanide and 10 c.c. of strong ammonia, in 500 c.c. of water, it is standardised by the usual process. The titration of the urine is carried out by adding to 100 c.c., 25 c.c. of solution A; the liquid is then filtered, and 20 c.c. of solution B, and a few drops of 20 per cent. potassium iodide solution containing 2 per cent.



of ammonia are added to 100 c.c. of the filtrate. The liquid is then titrated with N/10 silver nitrate solution, until a persistent turbidity is obtained. From the results, the quantity of xantho-uric compounds present may be readily calculated as uric acid. The process is applicable to urines containing albumin, but any iodide present must be removed by adding 1 c.c. of nitric acid and 20 c.c. of N/10 silver nitrate to 100 c.c. of the urine; the excess of silver nitrate is then precipitated by sodium chloride, the solution made up to 200 c.c. with water, and filtered. The uric acid is then determined in 100 c.c. of the filtrate by the process described above.

Test analyses gave very good results.

W. J. P.

**Composition and Analysis of Yeast.** By P. GUICHARD (*Bull. Soc. Chim.*, [3], 11, 230—239).—The author gives a summary of analyses of yeast made by various chemists.

Recently pressed yeast always loses about 72 per cent. of water at 120°, or by standing over sulphuric acid or calcium chloride; as it dries, the yeast loses its fermentative properties, but regains them under favourable conditions. The density of the yeast cells is about 1.181 at 16°, and was determined by shaking with a mixture of alcohol and chloroform, and adding one or other liquid until the yeast neither rose nor sank. Light petroleum extracts 1.4 per cent. of fatty matter from the dried yeast, which also contains 6.7—7.2 per cent. of ash. The author describes a new apparatus for determining the fermentative power of yeast.

W. J. P.

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## General and Physical Chemistry.

**Influence of Position-Isomerism on the Rotatory Power of Optically Active Compounds.** By H. GOLDSCHMIDT and S. FREUND (*Zeit. physikal. Chem.*, 14, 394—408).—The molecular rotatory power was determined for a number of isomeric compounds, chiefly derivatives of phenylcarbamic acid, and of dextrorotatory carvoxime. The results are contained in the accompanying table.

Compound.	Specific rotation.	Mol. rotation.
Amylic phenylcarbamate, $\text{CHMeEt} \cdot \text{O} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$ .....	+ 4.19°	+ 8.67°
Amylic orthotolylcarbamate, $\text{CHMeEt} \cdot \text{O} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_7\text{H}_7$ .....	+ 2.66	+ 5.88
Amylic metatolylcarbamate, " .....	+ 3.85	+ 8.51
Amylic paratolylcarbamate, " .....	+ 4.47	+ 9.88
Menthylic phenylcarbamate, $\text{C}_{10}\text{H}_{18} \cdot \text{O} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$ .....	- 77.21	- 212.33
Menthylic orthotolylcarbamate, $\text{C}_{10}\text{H}_{18} \cdot \text{O} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_7\text{H}_7$ .....	- 65.88	- 190.39
Menthylic metatolylcarbamate, " .....	- 71.43	- 206.44
Menthylic paratolylcarbamate, " .....	- 72.80	- 208.94
Carbanilidocarvoxime, $\text{C}_{10}\text{H}_{14} \cdot \text{NO} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$ .....	+ 31.67	+ 89.94
Carborthotoluidocarvoxime, $\text{C}_{10}\text{H}_{14} \cdot \text{NO} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_7\text{H}_7$ .....	+ 27.40	+ 81.65
Carbometatoluidocarvoxime, " .....	+ 29.79	+ 88.77
Carboparatoluidocarvoxime, " .....	+ 30.75	+ 91.64
Benzoylcarvoxime, $\text{C}_{10}\text{H}_{14} \cdot \text{NO} \cdot \text{CO} \cdot \text{C}_6\text{H}_5$ .....	+ 26.64	+ 71.66
Orthotoluylicarvoxime, $\text{C}_{10}\text{H}_{14} \cdot \text{NO} \cdot \text{CO} \cdot \text{C}_7\text{H}_7$ .....	+ 27.08	+ 76.64
Metatoluylicarvoxime, " .....	+ 26.86	+ 76.01
Paratoluylicarvoxime, " .....	+ 23.44	+ 66.34
Phenacetylcarvoxime, " .....	+ 40.63	+ 114.98
Orthobromobenzoylcarvoxime, $\text{C}_{10}\text{H}_{14} \cdot \text{NO} \cdot \text{CO} \cdot \text{C}_6\text{H}_4\text{Br}$ .....	+ 25.96	+ 90.34
Metabromobenzoylcarvoxime, " .....	+ 18.24	+ 63.48
Parabromobenzoylcarvoxime, " .....	+ 14.90	+ 51.85
Orthonitrobenzoylcarvoxime, $\text{C}_{10}\text{H}_{14} \cdot \text{NO} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ .....	± 0.0	± 0.0
Metanitrobenzoylcarvoxime, " .....	+ 20.68	+ 64.94
Paranitrobenzoylcarvoxime, " .....	+ 17.33	+ 54.42

It is noticeable that in most cases the value of the meta-compound falls between those of the ortho- and para-compounds, and that in the three last series of compounds the difference between the values of the meta- and para-compounds is approximately constant, namely 3.42; 3.34; 3.45 (*i.e.* for specific rotation). L. M. J.

**An Electrode Sensitive to Light.** By H. LUGGIN (*Zeit. physikal. Chem.*, 14, 385—393).—The author describes a form of electrode considerably more sensitive to light than any employed by previous investigators and gives a few details of its construction. It consists of a platinum plate covered with bromide of silver, and, when used, is paired with a similarly coated silver electrode in a decinormal solution of potassium bromide. The rise of potential is determined by a quadrant electrometer, and in some experiments

exposure to diffused daylight caused an increase of potential of 0.42 volt. The experiments show that when illuminated by weak light the rate of rise of potential is uniform and represented by a straight line until a maximum value is reached, after which it remains constant, or may fall slightly. With a stronger light, the rate of increase is more rapid, but the final value is not greater, the rate, however, is not directly proportional to the intensity of the light, but is proportionally less than for weak lights, whilst it is also lowered by previous exposure to a powerful light. Continuous and intermittent lights of the same mean intensity appear to have the same effect. The sensitiveness of the plate, however, does not remain constant, but, even after long rests, very different potential-increases are obtained with the same light.

L. M. J.

**Electrolysis and Polarisation of Mixtures of Salts.** By L. HOULLEVIGUE (*Ann. Chim. Phys.*, [7], 2, 351—384).—According to Buff, when a mixture of two salts is electrolysed there is always a fixed ratio between the amounts of each decomposed by the current, and this ratio is independent of the strength of the current used. In a former paper (*Abstr.*, 1890, 678) the author has shown that Buff's law is not strictly true, but is complicated by the probable occurrence of secondary actions, and further that if the secondary action is supposed to be proportional to the time, the ratio should be a hyperbolic function of the intensity of the current. In the present paper, it is shown that in the electrolysis of mixtures of zinc and copper sulphates the ratio Zn : Cu deposited does actually increase with the current and is a hyperbolic function of the intensity. Buff's law is therefore only approximately true when the intensity of the current is sufficiently great.

In the electrolysis of mixtures of variable composition, it is found that the weight decomposed of the more readily electrolysable constituent increases regularly with the amount in which it is added to the mixture, except when the total amount present is very small. Thus, if to a fixed amount of zinc sulphate, copper sulphate is added in amounts which increase in arithmetical progression, and the mixtures are electrolysed under comparable conditions, the weight of copper deposited also increases in arithmetical progression.

The polarisation produced in a mixture of two salts depends on the nature of the constituents, even when only one of them would undergo electrolysis. It diminishes in proportion to the weight of the more electrolysable constituent introduced into the mixture, except when the actual amount present is but small. Lippmann's law of the depolarisation of an electrode placed in a mixture containing one of its own salts only holds for very small currents.

The author shows that there is a theoretical relationship between the nature of the deposits produced by electrolysis and the corresponding polarisation.

H. C.

**Electrical Conductivity of Formic Acid.** By V. SAPOJNIKOFF (*J. Russ. Chem. Soc.*, 25, 626—631).—The electrical resistance of pure formic acid as determined by Hartwig appeared much too small

and was attributed by the author to the presence of considerable quantities of water in the acid. He therefore attempted to remove these as completely as possible, but found that, by recrystallisation, he could not obtain an acid melting above  $8.4^{\circ}$ . The conductivity of this acid, however, although it still contained traces of water, was only one-sixteenth of the conductivity of Hartwig's acid, namely  $0.4 \times 10^{-8}$  at  $18.8^{\circ}$ . J. W.

**Constitution of Inorganic Compounds.** By A. WERNER and A. MIOLATI (*Zeit. physikal. Chem.*, 14, 506—521).—The molecular conductivity of complex inorganic compounds, chiefly the double compounds of ammonia with salts of platinum, cobalt, &c., is employed as a means for elucidating their constitution. The salts may be divided into four groups, namely those in which the complex group is united with one, two, three, or four univalent ions respectively. The molecular conductivity ( $M_{1000}$ ) for the members of those groups which were examined gave the following results:—(i)  $96.7$ — $108.5$ , (ii)  $234.4$ — $267.6$ , (iii)  $383.8$ — $426.9$ , (iv)  $522.9$  (only one examined). The variation is greatest in the higher groups owing to less simple splitting into ions, but the difference between members of different groups is well marked, that is, about 140. The molecular conductivities of a large number of compounds are recorded and in a few cases depicted graphically. Changes in constitution, such as from purpureo- to roseo-salts, &c., by absorption of water, are indicated by increase in the conductivity, more or less rapid, according to the rate of hydration. The author then points out that dichroco-balt chloride (this vol., ii, 51) has a molecular conductivity at  $1^{\circ}$  of  $108.1$ , and must, therefore, be regarded as containing one chlorine ion, not three, as Jørgensen considered, but that, on standing, the compound passed by hydration into the compound with three chlorine ions. The effect of the substitution of water for ammonia in these classes of salts is also considered, and a table given. (Abstr., 1893, ii, 507.)

L. M. J.

**Determination of Transition Temperatures.** By E. COHEN and G. BREDIG (*Zeit. physikal. Chem.*, 14, 535—547).—The method described by Cohen (Abstr., 1894, ii, 340) is frequently inapplicable, owing to one of the saturated solutions becoming super-cooled and not changing at the transition temperature. A slight alteration in the apparatus is therefore made, so that instead of two saturated solutions, one only is employed, the other electrode being immersed in an unsaturated solution of the compound. At the transition temperature there must be a sudden change in the temperature co-efficient of the electromotive force, that is, in the value of  $\frac{dE}{dT}$ . The

apparatus employed is fully described, and experiments made with sodium sulphate are recorded. Curves are plotted with electromotive force as ordinate, and temperatures as abscissæ, and in each case sudden breaks are seen at the temperatures (1)  $33.8^{\circ}$ , (2)  $33.0^{\circ}$ , and (3)  $32.9^{\circ}$  respectively, the mean,  $33.2^{\circ}$ , agreeing satisfactorily with Cohen's previous determination,  $32.8^{\circ}$ , and with those of other

observers by other methods. The value of  $\frac{dE_2}{dT} - \frac{dE_1}{dT}$  is also calculated according to the equation  $\frac{dE_2}{dT} - \frac{dE_1}{dT} = \frac{W_2 - W_1}{T_0} \cdot \frac{nb_0}{2(b_0 - 10)}$ , where  $W_2$  and  $W_1$  are the heats of solution above and below  $T_0$ ,  $n$  the migration rate of the sodium ion, and  $b_0$  the number of molecules of water per molecule of the salt. Where two saturated solutions were employed, the value  $\frac{dE}{dT}$  has also the same value, and in both cases the calculated and observed result agreed well, thus—calculated 1.2;  $\frac{dE_2}{dT} - \frac{dE_1}{dT} = 1.3$ .  $\frac{dE}{dT} = -1.5$  millivolts.

L. M. J.

**Modifications of Beckmann's Ebullioscopic Apparatus.** By C. E. LINEBARGER (*Chem. News*, 69, 279—280).—To obviate the difficulties hitherto experienced when introducing the substance into the boiling solvent in the Beckmann ebullioscopic tube, the author does away with the side tube, fuses a piece of wider tubing on to the mouth, and fits this with a cork to take the thermometer and the end of the condensing tube, which is only 190 mm. long and 12 mm. in diameter, and being set upright, permits of any substance being dropped into the boiling solvent without risk of adherence to the sides. To minimise any escape of solvent during an experiment, the author suspends a small gilded copper surface condenser in the condensing tube, or closes the top of the latter with a cork carrying a small tube closed below and terminating above the cork with a capillary; in this tube some of the solvent is placed, and in the side of the tube, just above the liquid and below the cork, is a small perforation, so that any vapour escaping condensation has to pass by the perforation through this tube and capillary, before reaching the open air, and is therefore effectually condensed by the atmosphere already saturated with the vapour, and overflowing through the perforation is returned to the solution.

D. A. L.

**Thermodynamical Derivation of the Law of Van der Waals.** By G. BAKKER (*Zeit. physikal. Chem.*, 14, 456—466).—The author starts with three axiomatic propositions, namely, (1) that however high the temperature, the deviations from Boyle's and Gay Lussac's laws are finite; (2) that two fluid elements attract one another with a force which at any given temperature is dependent only on the masses and distances, and decreases rapidly as the distance increases; (3) the kinetic energy is a function of temperature. Employing then the equation  $T \left( \frac{dp}{dT} \right)_v - p = \left( \frac{de}{dv} \right)_T$ , he deduces first the expression  $p = T(fv) - \frac{a}{b^2}$ , and hence when the density is small,  $p = \frac{RT}{v-b} + \frac{a}{b^2}$ .

L. M. J.

**Specific Gravity of Aqueous Solutions.** By D. TURBARA (*Tras. Phys.-Chim. Soc. Sci. exper. Kharkoff*, 1893, Supp. 5, 1—315. In

Russian).—The author has made a series of specific gravity determinations with aqueous solutions of chloral hydrate, formic acid, acetic acid, propylic alcohol, and isopropylic alcohol. Pyknometers of capacities varying between 16 and 45 c.c. were employed, and a set of determinations was made in each case at 0°, 15°, and 30°, all numbers being referred to water at 4°. The author estimates his greatest error in the density to be  $\pm 0.00008$  to  $0.00009$ . The results obtained, when treated by the arithmetical and graphical methods of Mendeléeff and Pickering, indicate breaks corresponding with hydrates of definite composition, which show a general agreement with the hydrates found by other observers, although there occur many exceptions in detail. For example, while Pickering finds from the freezing points of solutions of propylic alcohol hydrates with 0.5, 1, 2, 7, 17, and 42 mols.  $H_2O$  to 1 mol.  $C_3H_7O$ , the author obtains hydrates with 2, 6, 18, and 36 mols.  $H_2O$  from a consideration of the specific gravity.

J. W.

**Determination of Vapour Densities; Production of a Vacuum.** By C. SCHALL (*J. pr. Chem.*, [2], 50, 87—88).—An improvement in the apparatus already figured and described (*Abstr.*, 1892, 553) is here depicted. The acid is now supplied to the carbonate in K (*loc. cit.*) through a stop-cock funnel sealed through the glass. The tube containing the substance whose vapour density is to be determined (D, *loc. cit.*) is attached to a small wire hook passing through a cork in the tube from the bulb; for this purpose, the said tube is not curved over as previously shown, but has a side tube sealed to it which serves for attachment to the vacuum pump.

To produce a vacuum without a mercury or water pump, the author passes the end of the tube (closed by a piece of rubber tube having a Bunsen valve in it) through which the exhaustion is to be effected, into a flask in which water can be boiled to expel the air, and which can then be closed so as to allow of the production of a vacuum by condensation.

A. G. B.

**The Volume Changes of Acids and Bases on Neutralisation.** By E. RUPPIN (*Zeit. physikal. Chem.*, 14, 467—485).—The author has investigated the volume changes when solutions of acids and bases are added in equivalent proportions, employing for the purpose Ostwald's modified form of Sprengel's pyknometer and using semi-normal solutions of the compounds employed. These consisted of the following acids:—Hydrochloric, nitric, chloric, iodic, perchloric, permanganic, acetic, ethylsulphuric, benzenesulphonic, methenedisulphonic, thiosulphuric, sulphuric, and hydroplatinohchloric, with the bases, ammonium, lithium, sodium, potassium, thallium, tetramethylammonium, tetramethylphosphonium, trimethylsulphonium, barium, strontium, and calcium hydroxides. In all cases, except when ammonium hydroxide was employed, the volume change was positive, and in all cases the agreement with Ostwald's law was satisfactory, that is, the difference between the changes of volume given by different acids with the same base had nearly the same value for all bases, and similarly for bases and an acid, the slight dis-

crepancies being due to incomplete dissociation. Tables are also given showing the differences in the volume change between ammonium and the other hydroxides with the various acids, and between acetic and the other acids with the various bases, this change being shown as an additive property of the ions present in the mixed solutions (see Abstr., 1893, ii, 417).

L. M. J.

**Influence of Pressure on the Properties of Solutions.** By G. TAMMANN (*Zeit. physikal. Chem.*, 14, 433—445).—Regarding the internal pressure of a solution to be given by the equation  $\pi = K + \Delta K + p$ , where  $K$  is the internal pressure of the solvent at zero external pressure, and  $p$  is the external pressure, the author points out that the alteration of physical properties may be connected with that of the internal pressure by the equation  $\Delta E = f(\Delta K + p)$ , and hence by the observation of the influence of external pressure on any property of a solution, the difference between the internal pressures of the solution and solvent may be determined. Finks' experiments on the influence of pressure on the electrical conductivity afford the necessary data, and from his results the values of  $\Delta K$  for sodium chloride, hydrogen chloride, and zinc sulphate solutions are determined and compared with those obtained from the isobar diagrams. The concordance is not very good, but is sufficient to justify the reasoning, especially in view of the magnitude of the probable errors. The corrections of the conductivity for internal pressure are given in the case of the same three salts, and the paper concludes with a short inquiry into the cause of the alteration in conductivity by pressure. It may be due to a change (1) in the number of free ions, or (2) in the internal friction between the ions and molecules of the solvent and dissolved substance. The second of these he considers the chief cause, as Röntgen's experiments show that in the case of water a pressure of 500 atmospheres has very little influence on the number of free ions. The author considers that Röntgen's conclusions, which are the reverse of these, are not justified by his experiments. In the case of water, unlike that of other liquids, the friction diminishes with increased pressure, and hence the conductivity increases, whilst the reverse must obtain with other liquids (see also this vol., ii, 224, 268, 342).

L. M. J.

**Osmotic Pressure of Solutions of Finite Concentration.** By T. EWAN (*Zeit. physikal. Chem.*, 14, 409—423).—The equation  $PV = RT$ , as applied to solution, is not absolutely correct, owing to the omission of many factors, one of the most important being the heat of dilution of the solution. The author calculates the relations between osmotic pressure, &c., when this is taken into account, employing, as a fundamental equation, Kirchhoff's relation between the heat of dilution and the vapour pressure  $-\frac{dQ}{dw} = \frac{RT^2}{JM_0} \frac{d}{dt} \log \frac{p_0}{p}$ ,

where  $Q$  is the heat of solution of 1 gram of the salt in  $w$  grams of water at  $T$  degrees absolute temperature,  $J$  is Joules' equivalent, and  $p_0$  and  $p$  are the vapour pressures of the solvent and solution respectively. An expression is first deduced connecting the vapour pressure

of the solution with its freezing point and heat of dilution, and the results are verified by means of sulphuric acid solutions ( $w$  varying from 1.826 to 16.825), the agreement between the observed and calculated results being entirely satisfactory. As in the expression,  $\log p_0/p$  is not independent of the temperature, it follows that v. Babo's law is only valid when the heat of dilution is zero. An equation connecting the osmotic pressure and temperature is next deduced, which, by omitting terms of small value, reduces to  $\frac{dP}{dt} =$

constant; that is, it is analogous to Ramsay and Young's gaseous formula  $p = bT + a$ . The effect of concentration is considered, and on the supposition that the equation should be of the form of that of Van der Waals, an expression is deduced  $-P(v-b) = RT + JM \frac{dQ}{dw}$ . The

values of the heat of dilution of various solutions of cane-sugar are finally calculated from the lowering of the freezing point, but the observed and calculated values do not show very good agreement.

L. M. J.

**Determination of the Molecular Weight of Soluble Compounds by means of Red Blood Corpuscles.** By W. LÖB (*Zeit. physikal. Chem.*, 14, 424—432).—A small quantity of the blood corpuscles are added to a solution of the salt or other compound contained in a small flask, which is then rapidly rotated for about three minutes, and the colour of the clear supernatant liquid noted. Two solutions are finally obtained of such strength that one is just coloured and the other not coloured, and the arithmetical mean is taken as that isotonic with the blood corpuscles. An estimation is similarly made with a solution of a salt of known molecular weight, and from this the required weight is obtained by the equation  $m = p \frac{cM}{PC}$ , where  $pP$ ,

$cC$ , and  $mM$  are the concentrations, isotonic coefficients, and molecular weights of the two compounds. The following isotonic coefficients are employed. Organic compounds as sugar, &c.,  $c = 2$ , and in salts the acid = 2, an alkali atom = 1, alkaline earth = 0. Details of the mode of preservation of the blood corpuscles are given, and the experimental results appended show that the method is one of considerable accuracy. It is available, however, only in the case of soluble compounds, and cannot be used for acids or bases; its advantage, when available, being the facility and rapidity of execution.

L. M. J.

**Historical Note on Isomorphism.** By J. H. VAN'T HOFF (*Zeit. physikal. Chem.*, 14, 548).—The author points out, in connection with Retger's recently published papers on isomorphism (this vol., ii, 348, and previous abstracts), that Buys-Ballot in 1846 (*Ann. Phys. Chem.*, 67, 433) drew attention to the fact that the chemical simplicity of a chemical compound was connected with the symmetry of its crystalline form, and adds a table by which this is clearly indicated.

L. M. J.



**Researches on Gas Reactions.** By M. v. RECKLINGHAUSEN (*Zeit. physikal. Chem.*, 14, 491—505).—The researches had for their object the volume alterations which occur during the reactions of gases, and the author in the first part of the paper describes the apparatus and methods employed for the purpose. By means of a style moving upon a rotating drum, the volume changes are directly recorded as a curve, with volume ordinates and time abscissæ. The gas mixtures employed were (1) hydrogen and chlorine; (2) carbonic oxide and chlorine; (3) ethylene and chlorine, of which the first two mixtures are sensitive to light, the third being unaffected by it. All the experiments were performed in diffused daylight, and the following results were obtained.

The mixture of hydrogen and chlorine expands at the moment of illumination, and this expansion then decreases, at first rapidly, then more slowly, until the original volume is reached, when the end of the action is indicated, and the whole mixture has been converted into hydrogen chloride. The expansion also diminishes before the end of the action, even if the mixture is protected from light; and the author considers it probable that the action continues in the dark. The second mixture behaves in a similar manner, but the final volume is only half the original. The third mixture, which is not sensitive to light, reacts, when suddenly mixed, without any initial expansion, which thus appears to be characteristic of the sensitive mixtures. He points out that the results differ from those of Bunsen and Roscoe, who observed no initial expansion, but leaves to further research the explanation of the difference.

L. M. J

**Velocity of Action in Non-Homogeneous Systems; Decomposition of Sulphuryl Chloride.** By G. CARRARA and I. ZOPPELARI (*Gazzetta*, 24, i, 364—370).—The velocity of interaction of sulphuryl chloride and water was studied by placing a layer of the chloride in a small beaker, pouring water on it, and suspending the whole in a larger vessel containing water; the contents of both vessels were kept stirred by means of a current of air, and samples were withdrawn for analysis from time to time. The results show that the action occurring in this non-homogeneous system is of the first order and obeys the same laws as actions of the same order in a homogeneous system. The velocity of action remains the same when decinormal potash is substituted for the water, thus indicating that the sulphuryl chloride is decomposed by the water, and not by the alkali.

W. J. P.

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## Inorganic Chemistry.

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**Nitramide.** By J. THIELE and A. LACHMAN (*Ber.*, 27, 1909—1910).—The authors have recently shown that urethane may be readily converted into nitrourethane,  $\text{NO}_2\text{NH}\cdot\text{COOEt}$  (this vol., i, 399). On the addition of potash dissolved in methylic alcohol to

a concentrated aqueous solution of this substance at  $0^{\circ}$ , *potassium nitrocarbamate*,  $\text{NO}_2\cdot\text{NK}\cdot\text{COOK}$ , separates in plates which are immediately decomposed by water with development of heat, yielding nitrous oxide and potassium carbonate. If, however, the salt is added to a mixture of ice and sulphuric acid, *nitrocarbamie acid* is set free, but at once splits up into carbonic anhydride and *nitramide*,  $\text{NO}_2\cdot\text{NH}_2$ . To isolate the latter, the solution is saturated with ammonium sulphate and extracted with ether; on evaporating the ether in a current of air at the ordinary temperature, the nitramide crystallises out in prisms; it may also be obtained in lustrous plates by adding light petroleum to the ethereal solution. It melts at  $72^{\circ}$ , but the melting point is considerably lowered by traces of moisture.

Nitramide is somewhat volatile at the ordinary temperature, and dissolves in all the common solvents with the exception of light petroleum, the aqueous solution having a strongly acid reaction. It is most unstable, and when mixed with copper oxide, lead chromate, or even glass powder, decomposes into nitrous oxide and water with development of heat. It is also decomposed by concentrated sulphuric acid and by hot water, but, unlike the alkyl nitramines, is equally unstable in alkaline solutions. On reduction, it yields a substance having strong reducing properties, probably hydrazine.

H. G. C

**Gaseous Nitrogen Trioxide.** By G. I. PORSHNEFF (*J. Russ. Chem. Soc.*, 25, 684—685).—From experiments, which are mostly confirmatory of older data, the author concludes that pure, dry nitrogen trioxide is incapable of existence in the gaseous state, the liquid substance on vaporisation decomposing into nitric oxide and nitrogen peroxide.

J. W.

**Chlorinated Boracites.** By G. ROUSSEAU and H. ALLAIRE (*Compt. rend.*, 118, 1255—1257).—The authors have prepared chlorinated boracites of the metals of the magnesium group by the method previously employed for the preparation of iron chloroboracite. The products contain from 0.8 to 1.2 per cent. of calcium, and with a view to avoid the presence of this metal, borax was used in place of boronatrocalcite, but, except in the case of zinc, the results were unsatisfactory. The wet and dry methods used by Heintz and by de Gramont for the reproduction of boracite also gave negative results, except in the case of zinc. The chloroborates are not obtained by the action of the vapours of the metallic chlorides on the corresponding boracites, which seems to show that the efficiency of boronatrocalcite is due to the sodium borate which it contains, this being converted into sodium chloride, which acts as a mineralising agent. This view is supported by the fact that pure calcium borate and boronatrocalcite, from which the sodium compound has been removed by washing, do not yield chloroborates.

All the substituted borates obtained crystallise in cubes, tetrahedra, and dodecahedra, and have a pseudo-cubic symmetry, but act on polarised light. Fouqué finds that the crystals are composed of aggregations identical in character with those of natural boracites.

The general formula of the chloroborates is  $6\text{M}''\text{O}, 8\text{B}_2\text{O}_3, \text{M}'\text{Cl}_2$ ,

The zinc compound crystallises in colourless tetrahedra and rhomboidal dodecahedra of sp. gr. 3.48; it is very stable, and is formed under a variety of conditions. It is obtained (1) by the action of zinc chloride vapour on borax at a dull red heat, (2) by adding boric acid and a small quantity of borax to a fused mixture of zinc and sodium chlorides, and (3) by the wet process of Heintz and de Gramont.

The cadmium, nickel, and cobalt compounds are prepared by passing dry chlorine over an intimate mixture of boronatrocalcite and the finely-divided metal, heated to redness. The cadmium compound is colourless, and crystallises chiefly in cubes, with some tetrahedra and cubo-octahedra; the nickel compound forms yellow tetrahedra and dodecahedra; the cobalt compound forms tetrahedra and cubes, violet by reflected, and green by transmitted light.

The manganese compound is obtained in white cubes by the action of chlorine on a mixture of boronatrocalcite and manganese carbide, the product being purified by treatment with concentrated hydrochloric acid, and any carbon being separated by means of bromoform and methylenic iodide.

The method which yields the substituted boracites gives much less satisfactory results when applied to the artificial production of ordinary boracite.  
C. H. B.

**Silicon Compounds.** By L. GATTERMANN and K. WEINIG (*Ber.*, 27, 1943—1948).—Gattermann (*Abstr.*, 1889, 342) has described a method whereby compounds of silicon are obtained from silicon prepared by reducing silica with magnesium powder. The production of these compounds depends on the temperature at which the action is allowed to take place; and in the present paper the authors specify the temperatures more carefully. A very convenient tube furnace is described in the original paper.

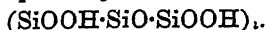
Silicon tetrachloride is obtained by the action of chlorine at 300—310°.

Silicochloroform is obtained by the action of hydrogen chloride at 450—500°.

Silicon hexachloride,  $\text{Si}_2\text{Cl}_6$ , is obtained from the crude silicon tetrachloride by fractional distillation; the yield amounts to 10 grams of  $\text{Si}_2\text{Cl}_6$  from 50 grams of crude chloride. It boils at 145—146°, and crystallises in large leaflets at -1°. When treated with dilute ammonia, it yields hydrogen and gelatinous silica. When the hexachloride is treated with chlorobenzene and sodium, silicontetraphenyl (m. p. 231°) is formed, and not siliconhexaphenyl. Since silicochloroform, under the same conditions, also yields silicontetraphenyl, it appears that in the silicon series there is a great tendency to form tetra-derivatives.

Silico-oxalic acid,  $(\text{SiOOH}\cdot\text{SiOOH})_2$ , is obtained as follows. The pure hexachloride is exposed in a platinum dish, cooled with ice, to the moisture of the air until it is converted into a solid, white mass. It is then allowed to remain over lime as long as hydrogen chloride is given off. The product contains 97 per cent. of silico-oxalic acid. When heated in a test tube, it decomposes violently with a feeble detonation. It also explodes when rubbed with a hard substance.

*Silicon octochloride*,  $\text{Si}_2\text{Cl}_8$ , is obtained from the residue of the fractional distillation of the hexachloride. It boils at  $210-215^\circ$ , has a vapour density corresponding with the formula  $\text{Si}_2\text{Cl}_8$ , does not solidify at  $-12^\circ$ , and is rapidly decomposed by water to form an insoluble acid, which is probably *silicomesowalic acid*,



This has strong reducing properties, and explodes much more violently than silico-oxalic acid.

E. C. R.

**Properties of Graphite obtained from Various Metals.** By H. N. WARREN (*Chem. News*, 69, 291).—Compared with graphite from iron, graphite obtained from nickel and cobalt is much finer; from ferro-manganese it is in thinner scales, less readily oxidised and brownish in colour; from manganese it is in still larger scales, distinctly brown, frequently translucent, and still less readily oxidised; from "chrome-eisen" the scales are much harder and brighter; from chromium they are more like silicon, with a semi-metallic lustre, and are oxidised with great difficulty. The character of the graphite depends, however, on the character of the fusion of the various metals; the varieties are, moreover, inter-convertible; thus, on introducing into molten iron, graphite from manganese, it acquires the properties of graphite from iron.

D. A. L.

**Refraction Constants of Organo-metallic Compounds.**  
**Atomic Refractions of the Elements.** By A. GHIEA (*Gazetta*, 24, i, 309—324; 324—327).—The author has determined the refraction constants of a number of organo-metallic compounds for the rays  $\text{H}_\alpha$ ,  $\text{H}_\beta$ ,  $\text{H}_\gamma$ , and D, and from the results has calculated the atomic refractions of the metals. The results for the line  $\text{H}_\alpha$  are tabulated below.

Substance.	Temperature.	$P \frac{\mu_{\text{H}_\alpha}^2 - 1}{d}$	$P \frac{\mu_{\text{H}_\alpha}^2 - 1}{(\mu_{\text{H}_\alpha}^2 + 2)d}$	Atomic refractions of the metals.	
				From $\mu$ .	From $\mu^2$ .
$\text{HgMe}_2$ .....	22.2°	41.09	23.96	23.29	12.76
$\text{HgEt}_2$ .....	23.2	56.97	33.13	23.97	12.81
$\text{HgPh}_2$ .....	22.7	114.20	64.39	26.80	13.55
$\text{HgNO}_3$ .....	10.3	36.0	20.5	20.72	11.66
$\text{SbCl}_3$ .....	16.4	53.09	32.24	23.69	14.18
" .....	20.0	54.67	31.07	25.27	13.01
$\text{SbPh}_3$ .....	14.0	162.61	93.96	31.51	17.70
$\text{SbPh}_3\text{Cl}_2$ ..	20.2	183.94	104.48	33.24	16.18
" .....	20.0	182.38	103.64	31.61	15.34
" .....	20.1	179.95	102.04	29.25	13.74
$\text{Pb}(\text{C}_2\text{H}_5\text{O}_2)_2$ ..	25.2	63.24	36.89	23.04	12.89
$\text{PbEt}_4$ .....	22.4	99.75	58.51	33.75	17.87
$\text{SnCl}_2$ .....	26.2	49.58	27.74	29.98	15.70
$\text{SnMe}_4$ .....	25.5	71.32	41.73	35.72	19.88
$\text{SnEt}_4$ .....	19.1	92.36	54.76	26.36	14.12

The refraction constants of mercurydiphenyl were determined in an 8.6 per cent. benzene solution, and those of mercurous nitrate in 13.9—21.22 per cent. nitric acid solutions. Antimony trichloride was examined in 13.5 and 22.05 per cent. benzene solutions respectively; triphenylstibene was examined in a 19.7 per cent. benzene solution, and its dichloride in 18.4, 20.6, and 22.5 per cent. benzene solutions respectively. The constants of lead acetate and stannous chloride were determined in 38.5 and 63.9 per cent. aqueous solutions respectively. All the other substances were examined in the pure liquid state; the molecular weights of the organo-metallic compounds were found to be normal by cryoscopic determinations in benzene solution. Many of the molecular refractions determined by the author differ considerably from those given by Gladstone (*Phil. Trans.*, 1870, i, 9).

W. J. P.

**Constitution of Combined Water in Organic Salts.** By B. KOSMANN (*Ber.*, 27, 1911—1912).—A reply to Surawicz (this vol., ii, 346), in which the author claims to have published similar conclusions in the year 1889, these being deduced from the "theory of hydration" proposed by him.

H. G. C.

**Constitution of Complex Metallammonium Bases.** By N. KURNAKOFF (*J. Russ. Chem. Soc.*, 25, 693—746).—In this paper the author collates and discusses in detail the various constitutions which have been attributed to the complex metallammonium bases. He is of opinion that the most reasonable formulæ for the salts are of types

such as  $M-a-Cl$ ,  $M\langle a \rangle Cl$ ,  $M\begin{array}{c} \diagup a \diagdown \\ a \end{array} Cl$ , &c., where M is an atom

of the metal, and a a molecule of ammonia, or of a similar compound.

J. W.

**Dimorphism of Potassium Fluoroborate.** By C. MONTENARINI (*Gazzetta*, 24, i, 478—480).—On adding to hydrofluoric acid, boric acid and then potassium carbonate, a gelatinous precipitate falls; this, when dried at 100°, is converted into very minute crystals of potassium fluoroborate belonging to the cubic system and showing the octahedron and dodecahedron.

The small, lustrous crystals, obtained by spontaneous evaporation of an aqueous solution of the salt, belong to the orthorhombic system,  $a : b : c = 2.7898 : 1 : 1.2830$ .

W. J. P.

**Action of Potassium Cyanide on Gold and on some other Metals and Minerals.** By G. A. GOYDER (*Chem. News*, 69, 262—263, 268—270, 280—281).—Minerals, not in a state of purity, but sufficiently freed from associated minerals to render any action of the latter insignificant, were crushed and sifted through a sieve with 30 holes to the linear inch; 10 parts of each crushed mineral was then placed in a stoppered bottle with 100 parts of a solution containing 1 per cent. of 91.5 per cent. potassium cyanide. The bottles were protected from light, shaken vigorously six times at intervals of an hour, and, after standing all night, the clear, supernatant liquid was examined for copper,

and for free potassium cyanide, with the following results expressed in grains per gallon.

Mineral.	Copper dissolved	Potassium cyanide remaining in solution.
Azurite .....	142·7	100·0
Malachite .....	148·4	6·5
Native copper .....	159·6	122·6
Copper glance .....	43·6	0·0
Copper pyrites.....	33·6	364·0
Iron pyrites .....	4·5	628·5
Quartz .....	—	656·2

Argentite was also dissolved, but iron and zinc sulphides were not. Cyanide solutions saturated with copper minerals did not dissolve gold. Lead, bismuth, antimony, arsenic, tin, cadmium, and mercury were exposed in a 6 per cent. solution of potassium cyanide, and were observed to dissolve with the absorption of oxygen, the action in some cases being very slow; magnesium, zinc, aluminium and copper, and cobalt, nickel, and iron reduced by hydrogen or carbonic oxide, under similar circumstances, dissolved with evolution of hydrogen, the quantity, in the case of copper, approximating to the change expressed by the equation  $\text{Cu}_2 + 4\text{KCy} + 2\text{H}_2\text{O} = \text{Cu}_4\text{Cy}_2 + 2\text{KCy} + 2\text{KHO} + \text{H}_2$ . But neither iron nor steel wire acted on potassium cyanide or aurocyanide. Other experiments confirmed the views generally entertained: (1) that the presence of oxygen is required to effect the solution of gold, &c., in solutions of potassium cyanide; (2) that under the influence of an electric current such solutions deposit their metallic contents, whilst the potassium cyanide gradually undergoes decomposition into potassium and ammonium carbonates, and that if the current is interrupted, the gold redissolves as long as sufficient potassium cyanide remains in solution.

D. A. L.

**Action of Sodium Peroxide on Iodine and on Lead Oxide.** By M. HOEHNEL (*Arch. Pharm.*, 232, 222—225).—When iodine (4 parts) is mixed with sodium peroxide (10 parts) and the mixture is locally heated, an action begins and spreads throughout the mass, a mixture of sodium hydrogen periodate,  $\text{Na}_2\text{H}_3\text{IO}_6$ , sodium iodide, and iodate being formed. The same products are obtained when sodium iodide is heated with sodium peroxide.

When lead oxide is mixed with water, and sodium peroxide added until the mass becomes white, sodium metaplumbate,  $\text{Na}_2\text{PbO}_3 + 4\text{H}_2\text{O}$ , is formed. It may be washed with 50 per cent. alcohol, and dried over oil of vitriol; it is white and crystalline; water decomposes it, yielding at first a yellow acid salt,  $\text{NaHPO}_3 + 3\text{H}_2\text{O}$ , but ultimately lead peroxide, which is also separated on treating the product with dilute acids. The author has obtained good results by using sodium peroxide for oxidising iron pyrites, but all crucibles are attacked during the process; a platinum crucible may lose 0·05—0·1 gram at each operation.

A. G. B.

**Solubility of Silver Chloride, Bromide, and Iodide in Inorganic and Organic Solvents.** By E. VALENTA (*Monatsh.*, 15, 249—253).—The following table gives the results obtained by the author.

Solvent.	Concentration.	100 grams of solution contain in grams		
		AgCl.	AgBr.	AgI.
$\text{Na}_2\text{S}_2\text{O}_3$ .....	1 : 100	0.40	0.35	0.03
	5 : 100	2.00	1.90	0.15
	10 : 100	4.10	3.50	0.30
	15 : 100	5.50	4.20	0.40
	20 : 100	6.10	5.80	0.60
$(\text{NH}_4)_2\text{S}_2\text{O}_8$ . . . . .	1 : 100	0.57		
	5 : 100	1.32		
	10 : 100	3.92		
$\text{Na}_2\text{SO}_3$ .....	10 : 100	0.44	0.04	0.01
	20 : 100	0.95	0.08	0.02
$(\text{NH}_4)_2\text{SO}_3$ .....	10 : 100	trace	trace	trace
$(\text{NH}_4)_2\text{CO}_3$ . . . . .	10 : 100	0.05		
$\text{NH}_3$ .....	3 : 100	1.40		
	15 : 100	7.58		
$\text{MgCl}_2$ .....	50 : 100	0.50		
$\text{KCN}$ .....	5 : 100	2.75	6.55	8.23
	5 : 100	0.08	0.21	0.02
$\text{NH}_4\text{SCN}$ .....	10 : 100	0.54	2.04	0.08
	15 : 100	2.88	5.30	0.13
$\text{KSCN}$ .....	10 : 100	0.11	0.73	
$\text{Ca}(\text{SCN})_2$ .....	10 : 100	0.15	0.53	0.08
$\text{Ba}(\text{SCN})_2$ .....	10 : 100	0.20	0.35	0.02
$\text{Al}_3(\text{SCN})_6$ .....	10 : 100	2.02	4.50	0.02
Thiocarbamide .....	10 : 100	0.83	1.87	0.79
Allylthiocarbamide .....	1 : 100	0.40	0.08	0.008
	5 : 100	1.90	0.35	0.05
	10 : 100	3.90	0.72	0.09

The author discusses the bearing of the above results on the practice of photography.

E. C. R.

**Hydrobromide of Cupric Bromide and a Red Cupric Potassium Bromide.** By P. SABATIER (*Compt. rend.*, 118, 1260—1263).—If a brown aqueous solution of cupric bromide is mixed with a concentrated solution of potassium, or calcium, or lithium bromide, a purple solution is obtained with a colour and absorption spectrum similar to those of solutions of cupric bromide in hydrobromic acid (this vol., ii, 352). The colour disappears in dilute solutions.

The view that the purple colour is due to the formation of anhydrous cupric bromide consequent on a dehydrating action of the hydrobromic acid or alkali bromide is untenable, because the colour is obtained with hydrobromic acid of the composition  $\text{HBr}, 5\text{H}_2\text{O}$ , and even with acid of the composition  $\text{HBr}, 12\text{H}_2\text{O}$  or

$\text{HBr}, 13\text{H}_2\text{O}$ . Moreover, the solutions in the concentrated acid lose their colour at  $100^\circ$ , but regain it on cooling. The solutions of the anhydrous bromide in absolute alcohol have an absorption spectrum which is independent of the proportion of bromide, and since the green hydrated bromide is efflorescent, it is unlikely that it would exist in presence of anhydrous alcohol; and, moreover, the alcoholic solutions when heated become more opaque, without any change of colour. The purple mixtures of cupric and sodium bromides when concentrated yield green crystals of the hydrate,  $\text{CuBr}_2 \cdot 4\text{H}_2\text{O}$ . It would seem probable, therefore, that the red-brown solutions really contain the anhydrous salt, whilst the purple solutions contain a hydrobromide or a double bromide.

When gaseous hydrogen bromide is passed into a concentrated aqueous solution of cupric bromide, black crystals of the anhydrous bromide separate, but their solubility seems afterwards to increase, and if the purple fuming liquid is cooled, it deposits black, lustrous crystals which readily decompose with evolution of hydrogen bromide, and which most probably have the composition  $\text{CuBr}_2 \cdot \text{HBr} \cdot 2\text{H}_2\text{O}$ , although the results of analysis agree more closely with the formula  $3\text{CuBr}_2 \cdot 2\text{HBr} \cdot 6\text{H}_2\text{O}$ .

When the mixed solutions of bromides are concentrated, they yield, as a rule, only crystals of the green hydrated cupric bromide, but the author has succeeded in isolating an anhydrous cupric potassium bromide,  $\text{CuBr}_2 \cdot \text{KBr}$ , in deliquescent, rhombic lamellæ, which are very opaque and almost black, but are red in very thin layers. The crystals seem to be monoclinic with the faces  $p$ ,  $h'$ ,  $g'$ , the angle  $p:h'$  being about  $65^\circ$ . When heated, the crystals give off one-third of their bromine, and melt to a black, very limpid liquid which solidifies to a greyish glass. The latter, when treated with water, yields potassium bromide and insoluble cuprous bromide. C. H. B.

**Stability of Aqueous Solutions of Mercuric Chloride.** By E. BURCKER (*Compt. rend.*, 118, 1345—1347).—The author has made observations similar to those of Vignon and Tanret (this vol., ii, 93) on the stability of aqueous solutions of mercuric chloride containing 1 part of the salt per 1000. He finds that ordinary spring water causes immediate decomposition of the mercuric chloride, and this decomposition continues under the combined influence of air and light, and the inorganic and organic substances contained in the water and in the air. Decomposition stops or becomes insignificant when the liquid is removed from the action of air and light. Solutions of mercuric chloride, prepared by means of pure distilled water, alter to only a very minute extent, even when exposed to air and light. C. H. B.

**Ternary Alloys containing Aluminium.** By C. R. A. WRIGHT (*Proc. Roy. Soc.*, 55, 130—139; compare *Abstr.*, 1893, ii, 522).—Cadmium is but slightly soluble in aluminium, and aluminium practically not at all in cadmium. Tin, however, acts as a solvent to both metals, and an examination of the ternary alloys that it forms with them shows that the aluminium-cadmium-tin critical curve is



depressed as regards the aluminium-lead-tin one, and probably also as regards the aluminium-bismuth-tin curve. Alloys of aluminium and lead (or bismuth), with antimony as solvent, show an excrescence in the central part of the critical curve, due to the separation of the difficultly fusible compound  $\text{SbAl}$ . The same reason causes an excrescence in the aluminium-lead-antimony curve, which is raised with respect to the zinc-lead-antimony curve, depressed as regards the aluminium-lead-tin one. An excrescence again appears, and for the same reason, in the aluminium-bismuth-antimony curve, which is depressed relatively to the aluminium-lead-antimony curve, and, like the zinc-bismuth-antimony curve, exhibits an inward depression at the point aluminium 65.22, bismuth 25.52, antimony 9.26 per cent., the ratio of bismuth to antimony corresponding with the alloy,  $\text{Sb}_2\text{Bi}_3$ . C. F. B.

**Analysis of an Ancient Slag.** By W. THOMASON (*Chem. News*, 69, 303).—The following are the numbers obtained from the analysis of a sample of slag, from the heaps long known as "Dud Dudley's slag," from the Netherton district of Staffordshire.

FeO.	Fe <sub>2</sub> O <sub>3</sub> .	MnO.	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O	SiO <sub>2</sub>
41.90	7.92	0.20	15.82	2.24	1.73	1.15	0.72	28.15
Total.		Sulphur		and		Phosphorus.		
99.83		0.024				0.424 per cent.		

The sample was vitreous with numerous blow-holes, and was evidently a product of an old direct process when the siliceous matter and gangue were slagged off as iron silicate without the addition of lime. D. A. L.

**Molecular Changes of Carbon and Iron accompanying the Tempering of Steel.** By G. CHARPY (*Compt. rend.*, 118, 1258—1260).—The author has compared the condition of the carbon as determined by Eggertz's method with the condition of the iron as indicated by the rectilinear break in the curve of extension under longitudinal strain. The proportion of carbon determined in this way is lower the harder the temper of the steel. Experiments were made with a number of bars from the same ingot of Siemens-Martin steel containing 0.71 per cent. of carbon. These bars were tempered by different methods, and their physical properties and the proportion of carbon (by Eggertz's method) were determined. When the bars were heated below 750° there was no change in the condition of the carbon, but in some cases there was partial modification of the iron, although no relation could be traced between this modification and the breaking charge. The increased resistance of the steel is probably due to change in its mechanical structure as shown by the fracture.

When the steel was tempered after heating above 740°, the iron and carbon showed simultaneous modification, the iron being completely transformed in all the bars that showed a breaking strain higher than 82 kilos. The proportion of carbon transformed diminished continuously as the breaking strain rose and the elongation

diminished. Bars with a breaking strain lower than 90 kilos. were readily attacked by files and other tools, and were not tempered in the proper sense of the word. Hard temper is accompanied by a high breaking strain and a reduction in the proportion of carbon as determined by Eggertz's method. C. H. B.

**Potassium Chlorochromate.** By G. HERFELDT (*J. pr. Chem.*, [2], 50, 93—94).—This salt is best prepared by dissolving 3 parts of potassium dichromate in 4 parts of concentrated hydrochloric acid by the aid of a gentle heat. Contrary to the statement of Heinze, the salt does not lose chlorine at 100°; this does not occur below 250°, and even after some hours' heating at 500—600° about 8 per cent. of the chlorine remains in the residue. The action of the salt on organic compounds is an oxidising one. An attempt to prepare chlorochromic anhydride by the action of chromyl chloride on chromic anhydride is described. A. G. B.

**Alkali Aurochlorides and the separation of the Alkalis.** By R. FÄBBERG (*Chem. Centr.*, 1894, i, 409—410; from *Nederl. Tijdschr. Pharm.*, 6, 1—4).—Sodium aurochloride,  $\text{NaCl} \cdot \text{AuCl}_3 + 2\text{H}_2\text{O}$ , is soluble in water, alcohol, and ether, and crystallises from all these solvents with the same amount of water of crystallisation. The potassium salt is not soluble in ether, and crystallises from alcohol without water of crystallisation. The lithium salt, when purified by washing with ether, contains  $4\text{H}_2\text{O}$ , and is not as stable as the sodium or potassium salts. The difference in solubility of these salts may be employed to separate sodium and potassium chlorides. Excess of gold chloride should be avoided, and the double salts must be dried at 100—110° to drive off all traces of acid, as these tend to make the potassium salt soluble in ether. These salts can also be employed for separating lithium and probably rubidium from sodium and potassium. L. T. T.

## Mineralogical Chemistry.

**Composition of Apophyllite.** By C. FRIEDEL (*Compt. rend.*, 118, 1232—1237).—Gentil found that apophyllite from Bou Serdoun, near Collo, Algeria, contained no fluorine, and the author confirms this statement. He also finds that this apophyllite, and five other specimens from widely different localities, when heated to redness give off water which has an alkaline, and not an acid, reaction. They contain small quantities of ammonia, part only of which is given off on heating to redness, and the remainder can be liberated by boiling with soda solution. Pisani has found that nine specimens of the mineral from different localities give off water which is neutral to test paper, whilst only one specimen from Feroe gave off water with an acid reaction.

Direct examination of several specimens for fluorine gave negative results, and the author concludes that, contrary to usual statements which seem to be based only on indirect evidence, this element is not an essential constituent of apophyllite. C. H. B.

**New Variety of Meteorite.** By G. HINRICHS (*Compt. rend.*, 118, 1418—1420).—The crust of meteorites is usually black, whilst the mass of the stone is greenish, the black crust having been produced by the action of heat, and its thickness indicating the depth to which this action has penetrated. A specimen which recently came into the author's possession has, on the contrary, a white crust whilst the mass of the stone is almost black. The crust consists of calcium sulphide,  $\text{CaS}$ . It can readily be produced artificially by holding a black fragment of the meteorite perpendicularly in a blowpipe flame just beyond the hottest point.

The mass of the meteorite has a mean composition agreeing closely with the pyroxene-tadgerite described by Menier. Its sp gr is 3.44. It contains 8 per cent. of meteoric iron, two thirds of which is in somewhat large grains, troilite in quantity almost as large as that of the iron, and pyroxene and peridote, the latter being present in larger proportion than the former. C. H. B.

**Analysis of the Meteoric Stone from Makariwa, near Invercargill, New Zealand.** By L. FLEISCHER (*Proc. Roy. Soc.*, 55, 142—145).—The meteorite, before weathering, contains nickel-iron, 5.20; olivine, 49.08; enstatite, 38.77; troilite, 6.00; schreibersite, 0.64; chromite, 0.31 per cent. Interest centres chiefly in the method of analysis, which is to be described in full in the *Mineralogical Magazine*. A separation is first made by means of a magnet; but as the metal present is partly oxidised, it is necessary to extract the unattracted part with mercuric ammonium chloride (after estimating the sulphur and phosphorus in it), heat the residue to a dull red heat in a current of hydrogen, and again extract; metal and metallic oxide are thus removed. The silicate portion is only slightly affected by this treatment, but the troilite and schreibersite are largely affected, and it is necessary (by estimating the sulphur and phosphorus in the residue after extraction) to allow for iron and nickel that have passed into solution from these minerals. The residue is then extracted three times with hydrochloric acid (sp. gr. 1.06) on the water bath; this completely destroys the olivine, the silica of which is then removed by extraction with aqueous sodium carbonate containing a little soda. The residual undecomposed silicate, enstatite, is separately analysed. Various determinations of the alkalis were also made. C. F. B.

**Analysis of Water from the Hot Springs of Monte Irone, Abano.** By R. NASINI and F. ANDERLINI (*Gazzetta*, 24, i, 327—342).—A number of springs of hot water are found at Monte Irone; the temperature of the water is not the same at all the sources, but the maximum temperature was 87° on a cold January day. The water issues accompanied by gas which contains 75 per cent. of nitrogen.

11 of carbonic anhydride, 8—12 of methane and other hydrocarbons, and 1·7—2 per cent. of hydrogen sulphide. The water is slightly alkaline, and at 20°/4° has the density 1·0026. The quantities of the various dissolved substances are given in the following table in parts per 10,000 by weight.

Substance.	Parts per 10,000.	Substance.	Parts per 10,000.
NaCl.....	84·0294	KCl.....	1·5332
NH <sub>4</sub> Cl.....	0·1165	LiCl.....	0·0128
MgCl <sub>2</sub> .....	3·0674	MgBr <sub>2</sub> .....	0·0973
MgI <sub>2</sub> .....	0·0640	NaHCO <sub>3</sub> .....	1·4824
CaH <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> .....	0·8970	FeH <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> .....	0·0116
CaSO <sub>4</sub> .....	12·6310	Al <sub>2</sub> O <sub>3</sub> .....	0·0015
SiO <sub>2</sub> .....	0·6639		

Total solid residue dried at 180° = 53·4850.

Traces of organic matter, boric acid, strontium, manganese, arsenic, and phosphoric acid are also present.

W. J. P.

## Physiological Chemistry.

**Respiration Apparatus**, by F. HOPPE-SEYLER (*Zeit. physiol. Chem.*, 19, 574—589); **Respiration in Man**, by E. LAVES (*ibid.*, 590—602); **Respiration in Cases of Diabetes Mellitus**, by W. WEINFRAUD and E. LAVES (*ibid.*, 603—628); **Respiration in a Dog after Extirpation of the Pancreas**, by the same (*ibid.*, 629—646).—The apparatus used in the investigations above quoted is one adapted for human beings on the principle of Regnault's well-known one. Its construction is illustrated by figures. In a normal individual, the average figures obtained from seven experiments, each of which is given fully, are the following.

Oxygen used, per diem.....	400·7 litres
"    per kilo. per minute.....	4·107 c.c.
Carbonic anhydride produced per diem....	324·5 litres.
"    "    "    per kilo. per minute.....	3·52 c.c.
Respiratory quotient.....	0·857

The results obtained in a diabetic patient show that the amount of oxygen consumed is about the same as in a healthy individual; the respiratory quotient is a little lower. The administration of carbohydrate food, selected so as to cause no corresponding output of sugar in the urine, causes an increase in the production of carbonic

anhydride and a rise of the respiratory quotient as in the case of healthy individuals.

In the dog, no noteworthy differences in the respiratory exchange were observable after extirpation of the pancreas. W. D. H.

**Estimation of the Acidity of the Stomach.** By P. MOHR (*Zeit. physiol. Chem.*, 19, 647—650).—A few experiments are recorded in which G. Töpfer's method of estimating the acidity of the contents of the stomach (this vol., ii, 262) was used. They show that the method is trustworthy. W. D. H.

**Lymphagogues.** By E. H. STARLING (*J. Physiol.*, 17, 30—47).—The formation of lymph is considered by Heidenhain to be due to a process of secretion by the endothelial cells of the vascular wall; and lymphagogues are substances which cause an increased flow of lymph. These may be divided into two classes; the first class includes substances like peptone and leech extract, which cause an increased flow of more concentrated lymph; the blood plasma is diminished both in quantity and concentration. The second class includes sugar, salt, and other crystalloids; they cause an increased flow of more watery lymph; the blood at the same time becomes more watery also, so that the excess of lymph is derived from the tissues.

An examination of the experiments on which these views rest has led the author (*J. Physiol.* 16, 224) to hold that lymph formation is not a vital secretory process, but that it can be explained by mechanical factors, difference of blood pressure, &c.; and the present paper is devoted to a fuller exposition of this view with fresh experiments in which lymphagogues of both classes were used. It is held that the differences in lymph flow can all be explained as due to differences in intracapillary pressure and permeability of the vessel walls. An important point strongly insisted on, is that arterial pressure is no measure of intracapillary pressure, but must be considered in relation to the pressures in the outlet from the capillary area, that is, in the veins.

Members of the second class of lymphagogues on injection into the blood attract water from the tissues and cause a condition of hydræmic plethora with increased capillary pressure. The increased lymph flow from the thoracic duct is due to the increased pressure in the abdominal capillaries.

Members of the first class of lymphagogues are really poisons which affect injuriously (1) the endothelial cells of the capillaries, especially in the liver, increasing their permeability; (2) the muscular walls of the blood vessels, especially in the splanchnic area, producing vascular dilatation; and (3) the heart muscle. The increased lymph flow is almost entirely due to the increased permeability of the hepatic capillaries. W. D. H.

**Physiological and Therapeutic Effects of the Homologues of Quinine.** By E. GRIMAUD, LABORDE, and BOURRU (*Compt. rend.*, 118,

1303—1306).—The authors have investigated the toxic and therapeutic effects of cupreine,  $C_{15}H_{21}N_2O \cdot OH$ , quinine (methylcupreine),  $C_{15}H_{21}N_2O \cdot OMe$ , and their higher homologues up to and including amylcupreine. Both toxic and therapeutic effects increase with the molecular weight. Ethylcupreine is a more powerful febrifuge than quinine, and propylcupreine may be useful in cases of high fever, but its toxic action is so powerful that it can only be administered in small doses. C. H. B.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Influence of Fluorine Compounds on Beer Yeast.** By J. ERFRENT (*Compt. rend.*, 118, 1420—1423).—The author has compared the chemical effects of ordinary yeasts and of yeasts inured to the action of fluorine compounds (this vol., ii, 62). For a given quantity of alcohol formed, the quantity of carbonic anhydride liberated is always distinctly higher with the ordinary yeast. For a given quantity of glucose decomposed, the quantity of alcohol formed is distinctly higher, and the quantity of glycerol and succinic acid lower, with the yeast inured to fluorine compounds than it is when ordinary yeast is employed. C. H. B.

**Constituents of the Tissues of Fungi.** By E. WINTERSTEIN (*Zeit. physiol. Chem.*, 19, 521—562).—In this research, numerous members of the fungus group were investigated by methods similar to those employed by E. Schulze. The chief constituent is undoubtedly a substance which resembles cellulose, and in some of its properties the true cellulose of Schulze (this vol., ii, 250); hemicellulose appears to be present, and can be extracted by means of hot, dilute acids. The fungus-cellulose ("Pilzcellulose") of de Bary is a mixture of cellulose with some nitrogenous substance, which, however, is not proteid in nature. Full references are given to previous work on the subject. W. D. H.

**Alkaline Reaction during Assimilation in Aquatic Plants.** By O. LOEW (*Chem. Centr.*, 65, i, 510; from *Flora*, 77, 419).—According to Hassack, the alkalinity produced by various aquatic plants is due to the hydrogen calcium carbonate in the nutritive solutions, and the production of normal carbonate, due to a separation of alkali by the plant. The author, however, in the case of elodea, observed that not only solutions containing calcium hydrogen carbonate became alkaline, but also those containing calcium nitrate. This was not due to ammonium carbonate, as no ammonia was present. Elodea also gradually reddened a solution of phenolphthalein in distilled water, and in eight hours calcium could be detected in the solution; organic matter was also detected. It is concluded that the reddening of

phenolphthalein is caused either by some organic calcium compound, or that calcium carbonate is held in solution in a colloidal state by the separated organic matter, and that this has the power of reddening phenolphthalein. A similar result was, in fact, obtained by shaking a warmed solution of calcium hydrogen carbonate with some gum arabic and phenolphthalein in a capacious flask until the loosely combined carbonic anhydride had separated. N. H. M.

**Oats Manured with Ammonium Sulphate.** By C. MITRAKEV (*Chem. Centr.*, 65, i, 560; from *Inaug. Diss.*, Leipzig, 1892).—Exclusive nitrogenous manuring increased the proteids and lowered the quantity of fat and non-nitrogenous extract of the grain. The varieties of oats which gave the greatest yield had larger grains, but were poorer in proteids than the other varieties. Heavy grains are richer in proteids than light grains. The small grains produced on rich soil are richer in proteids than the larger grains, whilst in the case of poor soil the reverse holds good. Increase in amount of proteid goes with decrease of fat and non-nitrogenous extract.

N. H. M.

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## Analytical Chemistry.

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**Electrolytic Estimation of the Halogens.** By G. VORIMANN (*Monatsh.*, 15, 280—284).—A dense reguline deposit of silver haloïd is obtained when a halogen is deposited on a weighed silver plate from an alkaline solution. The solution of the halogen is mixed with a few grams of alkali tartrate and 10 per cent. sodium hydroxide solution, and subjected to a current of 2 volts and 0.03—0.07 ampère. A platinum cathode is employed, and an anode of pure silver. The end of the electrolysis is determined when a new anode placed in the solution does not gain in weight. The anode after being removed from the solution, is washed with water, and then with alcohol, and dried over a Bunsen burner; finally it is heated until the silver haloïd darkens or melts, and is then allowed to cool, and weighed. If a very accurate estimation is required, it is necessary at the end of the operation to substitute a platinum electrode for the silver anode, and again pass the current for one hour, in order to deposit the small quantity of silver which is dissolved.

The results obtained by the author with potassium iodide are satisfactory. The iodine in a solution as iodate may also be determined by this method. E. C. R.

**Detection of Traces of Chlorine.** By A. VILLIERS and M. FAYOLLE (*Compt. rend.*, 118, 1413—1414).—The sensitiveness of the reaction previously described (this vol., ii, 396) varies considerably with different specimens of aniline, and is highest when the aniline contains small quantities of toluidine. By using orthotoluidine in

place of aniline (*loc. cit.*), an intense blue coloration is obtained, becoming violet-red on heating or after some time. The reaction is very distinct with as little as 0.1 milligram of chlorine.

When bromine is present, if orthotoluidine is used alone, it has the disadvantage that the precipitate produced by the bromine does not remain perfectly white. This difficulty is removed by employing as the reagent a mixture of a saturated aqueous solution of aniline (100 c.c.), saturated aqueous solution of orthotoluidine (20 c.c.), and glacial acetic acid (30 c.c.). So long as the reagent is in excess, no bromotoluidine is formed, but the bromine is converted into the stable and perfectly white bromaniline.

The action of chlorine on orthotoluidine in acid solution seems to be a rapid and easy method of preparing safranines.

Chlorine water may be used as a test for the presence of toluidine in aniline; if the latter is pure, the coloration will be brownish, but if the former is present in not too small quantity, the coloration will be first blue and then violet.

C. H. B.

#### Estimation of Chlorides in Products of Organic Origin.

By G. MEILLÈRE (*J. Pharm.*, [5], 29, 497—499).—When chlorine has to be estimated in organic products, it is necessary to burn off the organic matter, but this always causes an appreciable loss of chlorine.

The author recommends the following process. The substance (urine, for instance) is mixed with an equal bulk of 20 per cent. solution of calcium nitrate and evaporated to dryness in a flat-bottomed platinum dish; a slight elevation of temperature suffices to completely burn off the carbonaceous matter. The residue when treated with water yields a filtrate which is free from phosphates; to this a drop of solution of tropeolin is added, and then dilute sulphuric acid to acid reaction. A little powdered chalk is now added to decolorise the liquid, and the chlorine is titrated with silver nitrate, using potassium chromate as indicator. It is advisable to make a blank experiment.

L. DE K.

**Separation of Chlorine from Bromine.** By R. ENGEL (*Compt. rend.*, 118, 1263—1265).—1 to 2 grams of the substance is dissolved in 150—200 c.c. of water, mixed with 3 to 5 grams of ammonium persulphate, and heated at 70—80°. A current of air is passed into the liquid for about an hour in order to remove the bromine, which is best collected in a solution of sulphurous acid and estimated as silver bromide. It is not advisable to collect the bromine in potassium iodide solution, since small quantities of ozone, or possibly of persulphuric anhydride, may be given off. Under the conditions specified, the quantity of chlorine liberated from solutions of chlorides is very minute, and probably does not exceed 0.1 milligram.

Iodine can also be separated by means of ammonium persulphate, the cold liquid being mixed with sodium acetate and the persulphate, and the iodine removed by means of carbon bisulphide. Under these conditions, no trace of bromine or chlorine is liberated.

C. H. B.



**Detection of Hydrobromic acid.** By A. VILLIERS and M. FAYOLLE (*Compt. rend.*, 118, 1265—1268).—The well-known method of detecting bromides in presence of iodides, by liberating the two halogens successively by gradual addition of chlorine water, gives unsatisfactory results, owing partly to the fact that some bromine is liberated while iodides still remain undecomposed, and partly to the formation of iodine bromide. The brown coloration following the violet cannot be distinctly recognised when the quantity of bromine present is less than one-tenth of the quantity of iodine. In complete absence of iodine, however, a very distinct yellow coloration is imparted to carbon bisulphide by 1 milligram of bromine.

In order to remove iodine, the liquid, which should be free from nitric acid, is mixed with an excess of ferric chloride solution containing no free chlorine. About 5 c.c. of a half-normal solution should be added for every 0.1 gram of iodine supposed to be present. The liquid is evaporated to dryness on a water bath, and heated for an hour or two, in order to ensure complete volatilisation of the iodine. The residue is dissolved in a small quantity of water, the iron precipitated by means of an alkali, and the filtrate acidified with hydrochloric acid and treated with chlorine water and carbon bisulphide.

In the ordinary course of an analysis, it would be best to operate on the precipitate of silver haloid salts, hydrocyanic acid having been previously removed (this vol, ii, 396). The silver precipitate is heated with hydrogen sulphide, and the liquid concentrated after removal of the excess of the gas.

In order to detect bromine in iodine, the halogens must first be converted into the hydracids by treatment with hydrogen sulphide in presence of water.

C. H. B.

**Estimation of Iodine.** By A. VILLIERS and M. FAYOLLE (*Compt. rend.*, 118, 1332—1335).—The solution, which must be free from nitric acid, is mixed with ferric chloride solution containing no free chlorine (5 c.c. of a half-normal solution for every 0.1 gram of iodine), and agitated with carbon bisulphide. The latter is then drawn off, and a fresh quantity is added and agitated with the liquid, the process being repeated until the carbon bisulphide remains colourless. As a rule, four washings suffice. The several quantities of the bisulphide are mixed, washed with a little water to remove any traces of ferric chloride, and the iodine estimated with sodium thiosulphate solution.

A convenient form of apparatus for extracting with carbon bisulphide and washing the latter, consists of two cylindrical bulbs separated by a stop-cock. The upper end of one bulb is fitted with a glass stopper, and the lower end of the other is provided with a second stop-cock.

The chlorine, bromine, and iodine may be precipitated as silver salts, which are then decomposed by means of hydrogen sulphide and the excess of the latter expelled, the filtrate being treated in the manner described.

C. H. B.

**Detection of Iodine in Urine.** By H. SANDLUND (*Arch. Pharm.*, 232, 177—183).—Of the methods recommended for the detection of iodine in urine (see Neubauer and Vogel, "*Hamanalyse*") the author finds the following to be the most delicate and trustworthy: To 5 c.c. of the urine there are added successively 1 c.c. of sulphuric acid (1 : 4), 1—3 drops of dilute sodium nitrite solution (1 : 500), and carbon bisulphide or chloroform; after agitation, the solvent will be coloured rose-red by a smaller proportion of iodine than 0.001 per cent.; indeed, if a comparison with a tube containing urine known to be free from iodine be made, as little as 0.0000765 gram of iodine in 5 c.c. of urine can be detected by this test.

The two methods which the author has devised for the quantitative estimation of iodine in urine are as follows, the second being recommended for very small quantities of iodine, on account of the fact that filtration is avoided: 1.—25—50 c.c. of the filtered urine is acidified with nitric acid, and sufficient silver nitrate is added to precipitate all the iodine; after half-an-hour's digestion, the precipitate is collected, washed, and transferred, with the paper, to a flask, in which it is heated with water (8 c.c.), hydrochloric acid of sp. gr. 1.124 (4 c.c.), and zinc dust (2 grams). When reduction is complete, the contents of the flask are filtered into a distillation flask, and the filtrate is distilled with ferric chloride (3—4 grams), the distillate being received in a solution of potassium iodide, and the iodine titrated with a solution of sodium thiosulphate (N/50 or N/100) in the usual way. 2.—25—50 c.c. of urine (or more if the iodine content be very low) is evaporated to dryness in a platinum dish with sodium carbonate (0.25—0.5 gram); the residue is ignited to burn off organic matter, dissolved in water, and the solution, after being acidified with hydrochloric acid, is distilled with ferric chloride; the iodine is then determined in the manner described above. A. G. B.

**Estimation of Nitric acid.** By BARILLÉ (*J. Pharm.*, [5], 29, 441—444).—The author, remarking on an article by Henry (this vol., i, 252), states that, as long ago as 1878, he had proposed the use of the nitrometer for the estimation of nitrates in potable waters.

L. DE K.

**Application of Sodium Peroxide in Analysis.** By O. KASSNER (*Arch. Pharm.*, 232, 226—240).—The author has detected ozone in the oxygen which is evolved when sodium peroxide is dissolved in water, and attributes the activity of sodium peroxide as an oxidising agent to its presence. When sodium peroxide is added to a solution of uranyl nitrate, the yellow precipitate, which is at first formed, re-dissolves, and from the solution Fairley's sodium peruranate may be precipitated by alcohol. Whilst chromium hydroxide readily passes into solution as sodium chromate (Haussermann, *Abstr.*, 1893, ii, 471), manganous hydroxide is only oxidised to the hydrated peroxide, and ferrous hydroxide to ferric hydroxide. Upon these facts, the author bases a process for separating chromium from manganese and iron which is obvious (compare Clark, *Trans.*, 1893, 1079). If sodium peroxide is substituted for a mixture of sodium carbonate and potassium nitrate as an oxidant for manganese oxides, an excess must

be avoided, otherwise, on dissolving the product in water, the manganate will be reduced by this excess. Sodium peroxide may be substituted for hydrogen dioxide in the method described by G. Kassner (*Abstr.*, 1891, 245), which may be applied for the estimation of potassium ferricyanide. Cobalt is precipitated as black sesquioxide by sodium peroxide, but nickel remains as the green hydroxide; neither metal is precipitated by this reagent from a potassium cyanide solution. Mercury, gold, and silver salts are reduced to the corresponding metals by sodium peroxide; but the solutions of chloroplatinic and chloropalladious acids are not reduced, since their sodium salts appear to be stable; solutions of platinic and palladious chloride, obtained by adding silver nitrate to the acids, are, however, reduced.

For the quantitative separation of antimony, tin, and arsenic, sodium peroxide may be applied as follows. The mixed sulphides are stirred with about 30 c.c. of water, and sodium peroxide is added by degrees, until a small portion no longer gives a coloured precipitate on the addition of dilute sulphuric acid. The whole is then transferred to a silver crucible, evaporated to dryness, and kept in fusion for some time. The melt is treated with aqueous alcohol (3 : 1), and the undissolved sodium pyroantimonate collected on a filter and weighed as antimonyl antimonate. After the alcohol has been evaporated from the filtrate, this is acidified with dilute sulphuric acid, the precipitated stannic acid is dissolved by caustic soda, and carbonic anhydride is passed through the solution to incipient precipitation; ammonium chloride is then added, and the solution heated for half an hour to completely precipitate the stannic oxide, which is weighed as usual. The arsenic is precipitated from the second filtrate by magnesia mixture.

Qualitatively, the method may be modified by testing a small portion of the oxidised mixture (care having been taken that all the sodium peroxide has been previously decomposed by boiling) for antimony by adding a little of the liquid to some acidified potassium iodide solution; if antimony be present, it will be separated on adding alcohol after a somewhat prolonged digestion with sodium peroxide.

A. G. B.

**Separation of the Alkalis by means of their Aurochlorides.** By R. FASBENDER (*Chem. Centr.*, 1894, i, 409—410).—See this vol., ii, 421).

**A Test for Copper.** By P. SABATIER (*Chem. Centr.*, 1894, i, 657; from *Rev. intern. jaleif*, 7, 101; compare this vol., ii, 352).—If concentrated hydrobromic acid is added to a concentrated solution of cupric bromide, a violet-red hydrobromide is formed, which is but slightly affected by heating the solution, but is decomposed by dilution with water, with production of a blue coloration. If a solution containing a copper salt is added to 1 c.c. of concentrated hydrobromic acid, a purple coloration is produced if much copper is present, a lilac coloration if little. 0.1 milligram copper may be recognised by this test. A mixture of solid potassium bromide and concentrated phosphoric acid may be substituted for the hydrobromic

acid. The mixture should be slightly warmed, the coloration appearing on cooling.  
L. T. T.

**Estimation of Mercury in Presence of Iodine.** By FRANÇOIS (*J. Pharm.*, [5], 29, 493—497).—The author has proved that although mercuric iodide is not completely decomposed by heating with calcium oxide, it is when ignited with soda-lime. The analysis is conducted as usual, in a combustion tube, a little oxalic acid being added to the mixture to yield a current of hydrogen, which will assist in expelling the mercurial vapour. The soda-lime, which should have little tendency to fuse, is best prepared by slaking 4 parts of calcium oxide with 1 part of sodium hydroxide dissolved in 4 parts of water, and igniting the product. If it be desired to estimate the iodine also, the contents of the tube should be transferred to a generating flask, the delivery tube of which dips into a test glass containing a solution of silver nitrate. After first adding some water to slake the lime, nitric acid is *very* gradually added until the mass has dissolved; the traces of iodine which escape are absorbed by the silver solution. The liquid is then filtered, and the filter, after being moistened with a few drops of sulphurous acid, is well washed. Any free iodine in the filtrate is cautiously reduced by adding a little more sulphurous acid, and the iodine is then precipitated, using the silver nitrate solution from the test-glass. The results obtained by the author are very satisfactory.  
L. DE K.

**Volumetric Estimation of Gold.** By G. FRANZESCHI (*Chem. Centr.*, 1894, i, 657; from *Bull. Chim. Farmac.*, 1894, No. 2).—Excess of decinormal potassium oxalate is added to the solution containing the gold salt, the whole boiled for a few minutes, and then allowed to cool. The precipitated gold is collected, and the filtrate (to which 1 c.c. of dilute sulphuric acid is added) is warmed and titrated with decinormal potassium permanganate, 1 c.c. of decinormal potassium oxalate destroyed represents 0.0063 gram of gold. The gold solution must not contain free hydrochloric acid.  
L. T. T.

**Separation and Estimation of Small Quantities of Methylic and Ethylic Alcohols.** By L. PRUNIER (*J. Pharm.*, [5], 29, 407—410).—After the isolated alcoholic liquid has been treated with concentrated hydriodic acid to convert the alcohols into the corresponding haloid salts, the liquid is shaken with pure chloroform; or it may be distilled, and the first portions condensed in a receiver containing chloroform. After removing free acid by shaking with aqueous potash, the chloroform is agitated with a solution of silver nitrate and a little moist silver oxide, which, after some time, will cause a precipitate of silver iodide. This is washed, first with ammonia, and then with nitric acid, and weighed. If ethylic alcohol alone be present, its amount may be at once calculated from the weight of the silver iodide; but if both alcohols are present, their total amount must be ascertained from the specific gravity of the distillate, and their respective amounts calculated from the amount of silver iodide obtained.

The presence of methylic alcohol may be suspected when the chloroformic solution of the hydriodides boils below  $61^{\circ}$ , also by the alcohol yielding formic acid on oxidation. Ethylic alcohol, on the other hand, may be approximately estimated by determining the amount of iodoform it yields.

L. DE K.

**Iodometric Estimation of  $\beta$ -Naphthol.** By F. W. KÜSTER (*Ber.*, 27, 1905—1909).—The iodometric method of estimating  $\beta$ -naphthol, described by Messinger and Vortmann (*Abstr.*, 1890, 1473), only gives accurate results when the concentration of the  $\beta$ -naphthol solution is approximately constant, the amount of iodine fixed undergoing considerable variation when this is not the case. In order to determine the amount of  $\beta$ -naphthol in solutions containing from 0.1—0.5 gram per litre, the author made a large number of determinations with known and varying quantities of  $\beta$ -naphthol, using always 100 c.c. of the solution, 0.6 c.c. of 3.6 N soda, and 25 c.c. N/10 iodine; the amounts of thiosulphate required for titrating back were plotted into a curve, from which an interpolation table was drawn up, showing the amount of  $\beta$ -naphthol corresponding with any volume of thiosulphate solution used, and from this table the amount of  $\beta$ -naphthol in any solution can be determined accurately.

H. G. C.

**Testing Phenacetin.** By G. GUASTI (*L'Orosi*, 17, 111—115).—The usual test for the presence of acetanilide in commercial phenacetin consists in heating the suspected sample with soda and alcohol, and then warming with chloroform; if the characteristic odour of the isonitriles is detected, the sample is said to contain acetanilide. The author shows, however, that pure phenacetin gives the isonitrile odour under such circumstances; the test is therefore valueless.

The presence of 4 per cent. of acetanilide in phenacetin may be detected by boiling 0.5 gram of the sample with 10 c.c. of water, cooling, and filtering off the deposited phenacetin; the filtrate is concentrated, boiled with 1 c.c. of concentrated hydrochloric acid, and treated with a little liquid phenol and calcium hydrochlorite solution. On adding excess of ammonia, the liquid assumes an indigo-blue colour if acetanilide is present.

The following modification of Hirschsohn's method is sensitive to 0.5 per cent. of acetanilide in phenacetin. 1 gram of the sample is boiled with 15 c.c. of water, and the solution cooled and filtered. If acetanilide is present, the filtrate gives a turbidity with bromine water, due to the deposition of parabromacetanilide.

W. J. P.

**Estimation of Albumin by Méhu's Process.** By L. BULAND (*J. Pharm.*, [5], 29, 364—367).—Méhu recommends coagulating the albumin with phenol and washing the precipitate with a boiling, saturated solution of the same. The author, having tried the method, finds that a very appreciable amount of albumin is dissolved by the washings, but that no appreciable loss is incurred by washing with cold water containing 3—4 per cent. of phenol.

L. DE K.

## General and Physical Chemistry.

**Tautomerism.** By J. W. BRÜHL (*Ber.*, 27, 2378—2398; and *J. pr. Chem.*, [2], 50, 119—221). The experimental details are given in the latter paper only).—The author describes substances which contain the group :CH·CO as ketonic, whilst compounds containing the group :C·C(OH) are said to be “enolic.” It is difficult, by spectrometric methods, to find whether a ketonic form changes into an enolic form on rise of temperature, inasmuch as neither of the two ordinary expressions for the molecular refraction are quite independent of temperature changes. The molecular dispersion  $\left( \frac{n^2 - 1}{n^2 + 2} - \frac{n_1^2 - 1}{n_1^2 + 2} \right) \frac{P}{d}$  is, however, but very slightly affected by changes of temperature, and is therefore of great assistance in such problems. This expression for the dispersion is a highly constitutive one; if its value for a substance at a high temperature is the same as that at a low one, the constitution of the substance is certainly unaffected by the temperature change.

Position isomerides, such as the xylenes, have approximately the same molecular refraction; the differences between the molecular dispersions of aliphatic position isomerides are small, whilst the corresponding differences for aromatic isomerides are somewhat larger. The differences, however, become much greater for derivatives of substances of this class, which contain strongly refractive and strongly dispersive groups.

The results of the present investigation fully confirm the author's previous conclusion, that isomerides containing different kinds of double linkings, such as ethylenic and carbonylic ones, have very different refractive and dispersive powers. The ethylenic bonds have a greater spectrometric constant than carbonylic bonds, whilst the latter, in turn, have a greater optical value than the linkage C·O·C.

Aromatic and aliphatic monoketones, and 1:2- and 1:4-diketones, behave as true carbonyl compounds. The spectrometric behaviour of the 1:3-ketones is however anomalous; the same is true of acetophenone, and, in this case, is due to the proximity of the phenyl- and carbonyl-groups. Acetoformic (pyruvic) acid and acetopropionic (levulinic) acids have the molecular refractions and dispersions of true keto-compounds. This behaviour is quite different from that of acetoacetic acid; the methylic and ethylic salts of the latter, and of its methyl-, ethyl-, dimethyl-, and diethyl-derivatives are analogous in spectrometric behaviour. They are true keto-compounds, and not derivatives of hydroxycrotonic acid as Nef considers; acetoacetates, and mono- and di-alkylacetoacetates therefore have the constitutions  $\text{COMe} \cdot \text{CH}_2 \cdot \text{COOR}$ ,  $\text{COMe} \cdot \text{CHR}' \cdot \text{COOR}$ , and  $\text{COMe} \cdot \text{CR}'_2 \cdot \text{COOR}$  respectively. The spectrometric examination clearly shows that on introducing a carbethoxy-group into the acetoacetates or mono-alkylacetoacetates, the tautomeric or enolic form of the same type as the hydroxycrotonates is obtained; no reversion to the ketonic form

occurs on heating. A similar change in the acetoacetic nucleus probably occurs on treatment with bases; the so-called ethylic par-amidoacetoacetate is most probably ethylic imidobutyrate, whilst the action of phenylhydrazine on ethylic acetoacetate yields ethylic hydrazocrotonate.

Similarly, it is shown that ethylic oxalacetate is not a salt of keto-succinic acid but of hydroxyfumaric or hydroxymaleic acid; it therefore has the constitution  $\text{COOEt}\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot\text{COOEt}$ .

The salts of succinic, methylsuccinic, and malonic acids all behave optically as if they possessed the constitutions usually assigned to them; no evidence supporting the existence of the tautomeric enolic form sometimes attributed to malonic acid was obtained.

The spectrometric examination shows clearly that the substances hitherto regarded as ethylic acetomalonate, diacetomalonate, and ethylacetomalonate have quite different constitutions. The product of the action of ethylic chlorocarbonate on ethylic sodacetoacetate seems to have the constitution  $\text{COOEt}\cdot\text{O}\cdot\text{CMe}\cdot\text{CH}\cdot\text{COOEt}$ ; it is not identical, but isomeric, with the substance obtained by the interaction of acetic chloride and ethylic sodiomalonate; this has the constitution  $\text{OH}\cdot\text{CMe}\cdot\text{C}(\text{COOEt})_2$  or  $\text{CH}_2\cdot\text{C}(\text{OH})\cdot\text{CH}(\text{COOEt})_2$ . The former substance has a neutral reaction and does not colour ferric chloride, whilst the latter is strongly acid and gives an intense coloration with ferric chloride. Ethylic diacetomalonate is dienolic, having the constitution  $\text{C}(\text{CH}_2\cdot\text{C}\cdot\text{OH})_2(\text{COOEt})_2$ . Further, ethylic ethylacetomalonate contains no ethylenic bond, but has the constitution  $\text{CMeO}\cdot\text{CEt}(\text{COOEt})_2$ .

Acetylacetone has the constitution  $\text{OH}\cdot\text{CMe}\cdot\text{C}\cdot\text{CMe}\cdot\text{OH}$ ,

$\text{CH}_2\cdot\text{C}(\text{OH})\cdot\text{CH}_2\cdot\text{C}(\text{OH})\cdot\text{CH}_2$ , or  $\text{OH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{C}(\text{OH})\cdot\text{CH}_2$ ,

and does not seem to become ketonic on heating. Mesitylic oxide and phorone probably have the constitutions  $\text{CMe}_2\cdot\text{C}\cdot\text{CMe}\cdot\text{OH}$  and  $\text{CMe}_2\cdot\text{C}\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot\text{CMe}_2$  respectively.

The constitution assigned by v. Pechmann to ethylic acetonedicarboxylate is confirmed by the spectrometric results; acetylacetone and ethoxalylacetone are enolic compounds, having constitutions of the form  $\text{OH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{C}(\text{OH})\cdot\text{CH}_2$  and

$\text{COOEt}\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot\text{C}(\text{OH})\cdot\text{CH}_2$

respectively.

A spectrometric examination of several oxymethylene and carboxyl-derivatives of camphor and of pyrotritaric acid was also made; the latter substance would seem to have the constitution assigned to it by Paal and by Knorr, and is not a pentamethylene-derivative as supposed by Fittig.

W. J. P.

**Line Spectrum of Sulphur.** By A. DE GRAMONT (*Compt. rend.* 119, 68—71).—The line spectrum of sulphur, which is usually obtained by passing a condensed spark through sulphur vapour under low pressure, can also be obtained much more simply under ordinary pressure by passing a condensed spark between two platinum wires or two carbon rods covered with pure fused and cooled sulphur.

If the condenser is not used the sulphur inflames. Drawings of the spectrum and measurements of the wave-lengths are given. The groups in the red and green have a striated appearance which makes them easily recognisable.

Various natural metallic sulphides, when treated in the same way with a condensed spark, show the sulphur lines, although some of the groups may be masked by the lines proper to the metals present in the sulphides. C. H. B.

**Influence of Sodium and Ammonium Hydrogen Molybdates on the Rotatory Power of Rhamnose.** By D. GERNEZ (*Compt. rend.*, 119, 63—65).—The addition of small quantities of sodium hydrogen molybdate or ammonium hydrogen molybdate to aqueous solutions of rhamnose produces a relatively large increase in the rotatory power. When one-twelfth of a molecular proportion of the molybdate has been added, the observed rotation has nearly double its original value, but beyond this point the addition of further quantities of the salt produces relatively less and less effect. The addition of 6.75/24 of the molecular weight of the salt produces the maximum effect, the rotatory power  $[\alpha]_D$  being 22° 95 with sodium hydrogen molybdate, and 19° 91 with ammonium hydrogen molybdate. Further quantities of the salts produce no appreciable change. It is noteworthy that the maximum effect in the case of rhamnose is produced by the same relative proportions of the molybdates as in the cases of mannitol, sorbitol, and perseitol. C. H. B.

**Change of Sign of Rotatory Power.** By A. COLSON (*Compt. rend.*, 119, 65—68).—Pure amylic acetate, after fractionation over acetic anhydride, and the same product mixed with 1 per cent. of the anhydride, give the following rotations at different temperatures.

	-4°.	+16°.	60°.	78°.	100°.
Pure acetate....	0° 53'	1° 2'	1° 20'	1° 24'	1° 20'
Mixture.....	1 6	1 4	—	1 8	—

Pure amylic acetate seems to show all the characteristics of the internal congelation described by Le Bel (this vol., ii, 304), but the presence of a small quantity of acetic anhydride neutralises the effect of temperature. In view of the easy decomposition of ethereal salts, it is not improbable that the anhydride, by reason of its power of combining with water, gives stability to the molecule of the acetate, and hence brings about a condition of stable equilibrium in the liquid. This view is supported by the fact that acetylmaleic anhydride, which is both an acetate and an anhydride, shows the following rotations when pure and when mixed with 1 per cent. of acetic anhydride.

	60°.	40°.	30°.	18°.
Pure compound ..	-1° 32'	-1° 22'	-1° 18'	-1° 8'
Mixture .....	-1 29	-1 21	-1 18	-1 10

It follows that whilst there are compounds which have a rotatory power which varies greatly with the temperature, in some cases these variations are the result of variations in the conditions of chemical equilibrium. C. H. B.



**Variation of Rotatory Power with the Temperature.** By A. LE BEL (*Compt. rend.*, 119, 226—228).—A continuation of the discussion with Colson. The great variations in rotatory power with variations in temperature, observed in the case of methylic and ethylic tartrates, cannot be attributed to the presence of small quantities of tartaric acid and ethylic or methylic alcohol, and Ramsay has shown that at 70° ethylic tartrate consists of simple molecules.

C. H. B.

**Gas Batteries.** By F. J. SMALE (*Zeit. physikal. Chem.*, 14, 577—622).—The electromotive force was determined in the case of a large number of gas batteries, the electrode being usually platinum strips coated with platinum black, and immersed partly in the gas, partly in the electrolyte.

Experiments were performed to test the dependence of the E.M.F. on the nature and size of the plates and nature and concentration of the solutions. The nature of the plates had no effect, similar results being obtained with gold, platinum, and palladium, whilst a slight variation with the size, in the case of an oxygen-hydrogen chain, is explained by the slight absorption of oxygen by platinum black. The E.M.F. appeared to be independent of the electrolyte and its concentration, in the case of sulphuric, phosphoric, and chloracetic acids, and also, although less certainly, with sodium and potassium hydroxides, sodium sulphate, and potassium chloride. Abnormal values were, however, obtained with the halogen acids and many salts, which the author accounts for by the existence of secondary actions. Gaseous chains of hydrogen chlorine, hydrogen bromine, and hydrogen iodine were investigated, and the effect of dilution of a gas studied by the comparison of a hydrogen oxygen with a hydrogen air chain, the E.M.F. in the latter case being about 10 per cent. lower. The means of the result for the chains are—hydrogen oxygen, 1.044 volts; hydrogen chlorine, 1.532 volts; hydrogen bromine, 1.111 volts; hydrogen iodine, 0.530 volt. By immersing the electrodes in the same electrolyte at different concentrations, the electromotive force between the two solutions is found, and a number of tables with these results are recorded. The E.M.F. in the oxygen hydrogen chain falls regularly as the temperature increases, thus—0° = 1.090 volts, 20° = 1.065, 40° = 1.035, 60° = 1.001, and from these numbers the temperature coefficient of the solution tension is calculable, giving the result  $\frac{d\pi}{dt} = -0.00140$ ; that

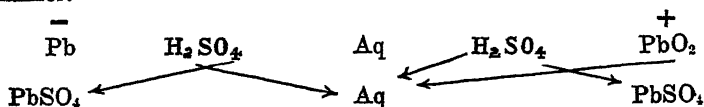
is the solution tension is inversely proportional to the absolute temperature. The E.M.F. with the similar electrode in an electrolyte at different temperatures was also observed and calculated, with fair agreement in the results. (See also this vol., ii, 305, 373.)

L. M. J.

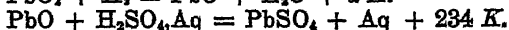
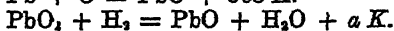
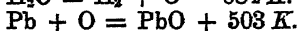
**Thermoelectric Heights of Antimony and Bismuth Alloys.** By C. C. HUICHINS (*Amer. J. Sci.*, [3], 48, 226—230).—The author has investigated the alloys of bismuth, antimony, and tin with the object of finding the best combination to use for the preparation of thermo-couples. The results show that the best results are obtained

when for the one element is taken bismuth containing 2 to 5 per cent. of antimony, and for the other bismuth with from 5 to 10 per cent. of tin. Both of these alloys are easily cast into very thin leaves, and are sufficiently tough to stand ordinary treatment. A junction of two very thin bars of bismuth with 2 per cent. of antimony, and of bismuth with 10 per cent. of tin gave an E.M.F. of  $10700 + 41 t$  in C.G.S. units. H. C.

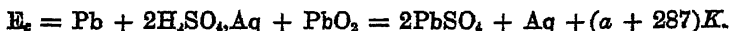
**Thermochemical Changes in the Secondary Cell.** By F. STREINTZ (*Monatsh.*, 15, 285—294).—The processes taking place in the secondary cell may be represented symbolically in the following manner.



They include the following reactions.



The chemical energy of the cell is obtained by adding these equations.



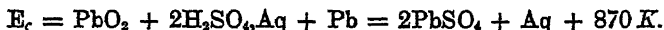
In order to find the value of  $a$ , the author selected the reaction



for thermochemical measurement. This gives



and it can be shown that  $a = (103 + c') K$ . The value found for  $c'$  was  $767 K$ , a value which, however, also includes the heat of solution of a small portion of the lead sulphate in hydrochloric acid. From this



The E.M.F. calculated from this is 1.885 volts, that directly observed being 1.900. H. C.

**Determination of Dielectric Constants.** By W. NERNST (*Zeit. physikal. Chem.*, 14, 622—663).—In the arms AB, AC of a Wheatstone bridge, two adjustable electrolytic resistances are placed; the two arms BC, CD contain two similar condensers consisting of two metal plates separated by a movable glass plate. The ends A, D are connected with an induction coil and B, C to a telephone in which silence or at least a minimum of sound occurs when  $R_{AB} : R_{AC} = C_{BC} : C_{CD}$ . A condenser consisting of a nickel or platinum trough with a fixed metal plate in the interior can be placed in either arm DB or

DC, and its capacity added to either of the measuring condensers, and this contains the liquid whose dielectric constant is to be measured. Minimum sound is then obtained by moving the glass of the measuring condenser. The arms DB, DC contain also auxiliary resistances, so that if the compound examined is not a perfect insulator its resistance can be also determined, since a minimum also results when  $R_{ab} : R_{ac} = R_{db} : R_{dc}$ . The condensers and other parts of the apparatus are calibrated once for all, and full details of the precautions, and a discussion of the probable errors, are given in the paper. The availability of the method is well seen by comparing the numbers which the authors obtained with it, and the determinations made by Landolt and Jahn (Abstr., 1893, ii, 57). In the case of 13 hydrocarbons, the mean difference is about 2 per cent, the results by this method being in almost all cases the higher. A number of measurements of the capacity of benzene, aniline, amyl alcohol, ethylic alcohol, and water at varying temperatures are also recorded; from the results, the temperature coefficients are calculated; the dielectric capacity in each case decreasing with increasing temperature.

L. M. J.

**The Influence of Pressure on the Conductivity of Electrolytes.** By I. FANJUNG (*Zeit. physikal. Chem.*, 14, 673—700).—The work of previous observers, especially Fink's, had shown that in the case of strongly dissociated compounds pressure affects the conductivity, probably owing chiefly to the alteration in the velocity of the ions. The author extends the observations to slightly dissociated compounds, and determines the conductivity of various organic acids and salts at concentrations varying from 1 to 1024 litres of solvent per gram molecule of dissolved substance, and at pressures varying from 1 to 260 atmospheres. The compounds examined were formic, acetic, propionic, butyric, isobutyric, lactic, succinic, malic, benzoic, and hydrochloric acids, and their sodium salts. In *all* cases, pressure caused a decrease in the electrical resistance, the alteration at 260 atmospheres varying from 6.55 to 9.02 per cent. in the organic acids, and from 1.23 to 2.92 per cent. in the more strongly dissociated compounds, corrections having been made for the compressibility of the solution. The rate of increase in conductivity is not constant; in most cases it decreases with increasing pressure. In the highly dissociated compounds, the alteration is most probably due to the diminution of the internal friction (see also this vol., ii, 410), and as the alteration of the fluid friction of water (1.2 per cent. at 260 atmos.) is comparable with the change in resistance of those solutions, it appears that an alteration of internal friction of the solvent is associated with an approximately equal alteration in the ionic friction. The value of  $\mu_{\infty}$  for the various pressures is also calculated, and hence by aid of the equations  $\mu^2/\mu_{\infty}(\mu_{\infty}-\mu)^2 = K$ , and  $100 RT\alpha \log K/dp = \Delta v$ , the volume alteration  $\Delta v$ , due to dissociation, can be deduced. This is done for the acids considered, and the results compared with those obtained by subtracting the volume increase on neutralisation from that obtaining with hydrochloric acid, the agreement of the results being remarkably close.

L. M. J.

**Decrease of Conductivity when the Water of Solution is displaced by Alcohol.** By C. SCHALL (*Zeit. physikal. Chem.*, 14, 701—708).—The conductivity of aqueous solutions of electrolytes is lowered by the addition of a non-electrolyte such as alcohol (Abstr., 1892, 1038) but to varying extents, hence acids at concentrations at which the conductivity is equal in aqueous solution give unequal values in alcoholic solutions. This is proved in the case of hydrochloric, picric, oxalic, and dichloroacetic acids, the conductivities of which were determined in solutions in water, methylic alcohol and dilute ethylic alcohol. If the velocity of the hydrogen ion greatly exceeds that of the combined ion, then, the author considers, the alteration is due chiefly to the change in degree of dissociation of the compound, which must, therefore, be widely different in alcoholic solutions at concentrations at which the dissociation degrees in water are equal. L. M. J.

**Specific Heat of Liquid Sulphurous Anhydride.** By E. MATHIAS (*Compt. rend.*, 119, 404—407).—The specific heat of liquid sulphurous anhydride has been directly measured by the author, at temperatures varying from  $-20^{\circ}$  to  $155.5^{\circ}$ . He finds that the true specific heat of the liquid is always positive and increases with the temperature. Between  $-20^{\circ}$  and  $+130^{\circ}$  the specific heat  $m$  is given approximately by the formula

$$m = 0.31712 + 0.0008507t + 0.000006762t^2.$$

H. C.

**Heat of Fusion of some Organic Compounds.** By L. BRUNER (*Ber.*, 27, 2102—2107).—This has been determined for the compounds mentioned below; the results of individual experiments never differed by more than 2—3 per cent. The numbers indicate the Calories given out by 1 gram of the substance on solidifying; those in brackets indicate the heat of fusion as calculated by van't Hoff's formula from the lowering of freezing-point caused by the same substance. It will be noticed that the heat of fusion of a bromo-derivative is less than that of the mother substance, or of the analogous chloro-derivative.

Methylic oxalate, 42.6. Crotonic acid, 25.3. Phenylacetic acid, 25.4. Bromal hydrate, 16.9. Stearic acid, 47.6 (49.2). Palmitic acid, 39.2 (49.5). Paradichlorobenzene, 29.9. Paradibromobenzene, 20.6. Metachloronitrobenzene, 29.4. Parachloronitrobenzene, 21.4. Orthonitrophenol, 26.8. Paracresol, 26.3 (26.0). Azoxybenzene, 21.6. Azobenzene, 27.9 (28.2). Parachloraniline, 37.2.  $\alpha$ -Naphthylamine, 22.3 (26.3). Benzophenone, 23.7 (21.5). Menthol, 18.9.

C. F. B.

**The Function  $\alpha$  in Van der Waals' Equation.** By G. BAKKER (*Zeit. physikal. Chem.*, 14, 664—670).—From thermodynamical equations is deduced the conclusion that the function  $\alpha$  in van der Waals' equation decreases with increase of temperature until a zero value is reached, and that the curve which expresses the relation of this function to the temperature is convex to the axis of temperature. The author points out further that these results are also proved by the

experimental observations, or at least are valid in the cases of hydrogen and carbonic anhydride. L. M. J.

**Relations between the Laws of Mariotte, Gay Lussac, and Joule.** By G. BAKKER (*Zeit. physikal. Chem.*, 14, 671—672).—Owing to a statement in Poincaré's "Cours de physique mathématique," that Joule's law does not follow necessarily from the other two laws, the author reduces the expressions to the following forms:—

Boyle's law,  $pv = f_1(T)$ ; Gay Lussac's law,  $e + pv = f_2(T)$ ; Joule's law,  $c = f_3(T)$ , in which case either follows as a necessary consequence from the other two. L. M. J.

**Gas Baroscope and its Applications.** By G. BODLÄNDER (*Ber.*, 27, 2263—2270, and *Zeit. angew. Chem.*, 14, 425—431).—The determination of the weight  $G$  of a gas is usually made indirectly by measurement of the volume  $V$  at the atmospheric pressure  $b$  and temperature  $t$ . If  $M$  is the molecular weight of the gas, then 1 c.c. weighs 0.0446725  $M$  and

$$G = \frac{V \times b \times 273 \times 0.0446725 \times M}{(1 + 0.0001614t) \times 760 \times (273 + t)} \text{ milligrams.}$$

Instead of varying the volume and pressure of the gas, it would be simpler, both for measurement and calculation, to bring the volume of the gas, by either compression or expansion, always to some constant quantity, so that the pressure alone would vary and be proportional to the amount of the gas. If the constant volume  $V$  is so selected that

$$V = \frac{(1 + 0.0001614t) \times 760 \times (273 + t)}{273 \times 0.0446725 \times 100} \text{ c.c.}$$

then 
$$G = \frac{bM}{100} \text{ milligrams.}$$

The gas baroscope is an instrument constructed on the above principle. It consists of a glass globe, closed above by a three-way stop-cock, and terminating below in a graduated tube which communicates with a mercury reservoir. The volumes of the globe and tube are so selected that the graduations give the values of  $V$  for temperatures varying from  $0^\circ$  to  $30^\circ$ , as calculated from the equation given above. The gas to be examined is introduced into the globe, and the height of the mercury in the reservoir so adjusted that its level in the graduated tube corresponds with the temperature of the gas. The gas is then expelled from the globe, which now remains vacuous, and the height of the mercury again adjusted so that the level of the mercury in the graduated tube is that maintained in the previous measurement. The difference between the heights of the mercury in the two cases gives the value of  $b$ , and  $G$  is then easily calculated. The gas baroscope may be used in all cases in which the weight of a gas has to be ascertained. Experiments are detailed in the papers in which it has been applied to the determination of nitrogen by Dumas' method, to the measurement of vapour densities, and to the

analysis of substances, such as carbonates and nitrates, which give rise to gaseous products of decomposition (see this vol., ii, 471).

H. C.

**Relation between the Density of a Saline Solution and the Molecular Weight of the Dissolved Salt.** By G. CHARPY (*Compt. rend.*, 119, 156—158).—In a previous paper (*Abstr.*, 1892, 765), in studying the densities of saline solutions, the author represents the concentration by the ratio of the number of molecules of the dissolved compound to the total number of molecules of the solution. The molecular weight of water was then taken as 18, but as Ramsay's recent investigations lead to the conclusion that the liquid molecule of water is greater than the gaseous molecule, the author has now recalculated his results, using in the one case  $3 \times 18$ , and in the other  $4 \times 18$ , as the molecular weight of water. He finds that for values very little higher than  $3 \times 18$ , the curves representing the densities plotted against the concentrations become straight lines, or in other words, if it is assumed that at  $0^\circ$  the molecular weight of water is about  $3 \times 18$ , the density of a saline solution is found to be proportional to the molecular concentration.

With the aid of this new and simple relationship, the question of the connection between the density of a saline solution and the molecular weight of the dissolved salt was further studied. A number of sulphates and chlorides were examined, and it was found that the densities of solutions of the same concentration (molecular) are in the case of analogous salts proportional to the molecular weights of these salts.

H. C.

**Density of Dilute Aqueous Solutions.** By F. KOHLRAUSCH and W. HALLWACH (*Ann. Phys. Chem.*, [2], 53, 14—42).—In order to determine the densities of dilute aqueous solutions to within a limit of error of  $10^{-4}$ , the authors have had recourse to the displacement method of weighing a ball of glass in the liquid under examination. The ball is suspended from an arm of the balance by means of a single cocoon fibre; its total weight was 133 grams, but when weighed in the solutions under examination its weight never exceeded 4 grams. In this way solutions of densities up to 1.03 could be examined. Great care was taken in measuring the temperature and in maintaining it constant during the carrying out of a determination, a greater variation than  $\frac{1}{100}^\circ$  being in no case allowed. A precise description of the apparatus employed for this purpose and its mode of arrangement is given in the paper.

Determinations were made with solutions of sodium chloride and carbonate, magnesium and zinc sulphates, hydrochloric, sulphuric, phosphoric, tartaric, acetic, and monochloroacetic acids, and cane sugar. Tables are given of the results obtained in each case. By combining the results with those obtained for concentrated solutions of the compounds examined by Gerlach, Marignac, Oudemans, and Kohlrausch, complete density tables for solutions of these compounds are obtained. From these, the molecular volumes  $\phi$  of the dissolved substances are calculated, on the assumption that the water undergoes no contraction in volume. The molecular volumes are found to

increase regularly with the molecular concentration, except in solutions containing less than  $\frac{1}{2}$  gram-mol. per litre of zinc and magnesium sulphates, sulphuric, phosphoric, tartaric, and monochloroacetic acids. With dilute solutions of these compounds, the molecular volume at first increases very rapidly, and it is only when the concentration exceeds that named, that the regular increase of the molecular volume with the concentration is observed. H. C.

**Viscosity of Solutions.** By G. JÄGER (*Monatsh.*, 15, 254—268).—The coefficient of viscosity  $\mu$  may be expressed by the formula  $\mu = 2\pi r^2 c / 3\lambda$ , where  $r$  is the radius,  $c$  the velocity,  $\lambda$  the mean length of the path of a molecule, and  $\rho$  the density of the solution. If  $v$  is the volume of the liquid under consideration, and  $b$  the space in the volume  $v$  actually filled with matter, the above expression becomes

$$\mu = \frac{4\pi r^2 c}{9 \left( 1 - \sqrt[3]{\frac{b}{v}} \right)}.$$

The coefficient of viscosity is also a function of the temperature  $\mu = f(t)$ , so that the coefficient of a solution that has a melting point reduction  $\Delta$ , is  $\mu_{\Delta} = f(t + \Delta)$ . Developing according to Taylor's theorem  $\mu - \mu_{\Delta} = -\Delta f'(t) - \frac{\Delta^2}{2} f''(t) - \dots$ . For water, the values of the function and its derivatives are calculated empirically from the experiments of Sprung, and the formula is then applied to aqueous solutions. The calculated results are found to be in general agreement with those obtained experimentally by Sprung. H. C.

**Saturated Solutions.** By A. ÉTARD (*Ann. Chim. phys.*, [7], 2, 503—574; compare Abstr., 1892, 398).—Determinations of the solubility of salts between 100° and 250° are conveniently made in a glass tube bent at 120° and constricted at the middle. The salt is placed in one arm, and the tube partly filled with water and sealed off; after heating, at a fixed temperature, in a bath containing a molten mixture of potassium and sodium nitrates, part of the solution is caused to run into the second arm of the bent tube, and is analysed when cold. Solubilities at temperatures above 250° are best determined by Guthrie's method.

The solubility,  $y$ , of a salt is taken by the author as the percentage of salt contained in the saturated solution; if  $p$  be the weight of salt, and  $p + \pi$ , the weight of solution in which it is contained, then  $y = \frac{100p}{p + \pi}$ . Using this scale of solubilities in place of the ordinary one, the curve connecting solubility and temperature lies wholly between 0 and 100 per cent. of salt; further, 100 on the  $y$ -axis corresponds with the melting point of the anhydrous salt on the other axis; the curve is also a curve of melting points of mixtures of dissolved substance and solvent.

The experimentally determined solubility curves usually consist first of a curved part, of which the continuation is one or more straight lines; the last of these passes through the "limiting" point,

or point of fusion of the anhydrous substance. The second column in the following table gives the equation to these straight line solubility curves, and the third column ( $t_1 - t_2$ ) gives the limits of temperature between which the equations hold; the solvent used was water.

Salt.	%.	$t_1 - t_2$ .
AgNO <sub>3</sub> .....	81.5 + 0.1340 <i>t</i>	60—198°
KNO <sub>3</sub> .....	24.0 + 0.7100 <i>t</i>	20—70
	59.5 + 0.3727 <i>t</i>	70—125
	80.0 + 0.0938 <i>t</i>	125—338
NaNO <sub>3</sub> .....	39.0 + 0.2825 <i>t</i>	—5—+64
	58.5 + 0.1666 <i>t</i>	64—313
Ba(NO <sub>3</sub> ) <sub>2</sub> .....	4.5 + 0.2025 <i>t</i>	0.4—175
KClO <sub>3</sub> .....	2.5 + 0.2060 <i>t</i>	0—50
	12.7 + 0.4230 <i>t</i>	50—150
	55.0 + 0.2163 <i>t</i>	150—358
Ba(ClO <sub>3</sub> ) <sub>2</sub> .....	19.0 + 0.382 <i>t</i>	0—100
KCl .....	19.6 + 0.1916 <i>t</i>	—11—+25
	26.5 + 0.1039 <i>t</i>	25—732
NaCl .....	25.8 + 0.0248 <i>t</i>	0—250
	<i>a</i> + <i>at</i>	250—772
BaCl <sub>2</sub> .....	25.5 + 0.1074 <i>t</i>	0—93
	35.5 + 0.0600 <i>t</i>	93—215
KBr .....	28.2 + 0.2700 <i>t</i>	—20—+38
NaBr .....	40.1 + 0.1314 <i>t</i>	—22—+51.5
	49.5 + 0.0690 <i>t</i>	51.5—230
KI .....	57.0 + 0.1090 <i>t</i>	0—111
	68.5 + 0.0618 <i>t</i>	111—638
NaI .....	59.5 + 0.1933 <i>t</i>	—5—+60
	74.0 + 0.0450 <i>t</i>	70—626°
CdI <sub>2</sub> .....	42.4 + 0.1154 <i>t</i>	—4—+97
	55.0 + 0.1076 <i>t</i>	97—366

The solubility curve of silver nitrate is a curved line between — 7 and + 60°, whilst the curve for potassium nitrate is slightly curved between — 3° and + 20°.

In addition to the above, the author has determined the solubilities of a large number of other salts, for which the original paper must be consulted. The solubility curves of mercuric chloride in water and in 13 organic solvents were determined; those for cupric chloride in 9 organic liquids. In these cases, just as in those of aqueous solutions, the solubility curves are composed of straight lines, the last of which points towards the melting point of the salt; evidence of the existence of numerous double compounds of these two chlorides with the solvent was obtained.

The curves of solubility of sulphur in carbon bisulphide, benzene, and ethylenic dibromide extend from the freezing point of the solvent to the melting point of sulphur. The solubility of sulphur in hexane was also determined.

W. J. P.



**Solubility of Inorganic Salts in Organic Solvents.** By S. v. LASZCZYNSKI (*Ber.*, 27, 2285—2288).—The author gives tables of the solubilities of copper chloride, mercuric chloride, mercuric iodide, cobalt chloride, stannous chloride, lithium chloride, lead iodide, potassium iodide, silver iodide, silver nitrate, bismuth nitrate and potassium thiocyanate in ethylic ether, ethylic acetate, acetone, amylic alcohol, benzene, aniline, and pyridine. E. C. R.

**Change of Free Energy on mixing Concentrated Solutions.** By W. NERNST (*Ann. Phys. Chem.*, [2], 53, 57—68).—The author shows that when two concentrated solutions of similar composition, but of different concentration, are mixed, the heat which is developed is generally a measure of the energy set free, or that generally the change in free energy is equal to the change in the total energy of the system. Thus, if the vapour pressures of the two solutions at the absolute temperature  $T$  are  $p_1$  and  $p_2$ , in order to transfer 1 gram mol. of water from the one solution to the other, the work required will be  $RT \log \frac{p_2}{p_1}$ , where  $R$  is equal to 2.00 if the work is expressed in gram-calories. This quantity should, according to the rule given above, be equal to the difference in the heats of dilution of the two solutions, if their concentrations only differ by the gram-molecule of water transferred. This is shown to be the case with certain solutions of sulphuric acid. H. C.

**Endothermic Reactions effected by Mechanical Force.** By M. C. LEA (*Zeit. anorg. Chem.*, 7, 50—51).—Referring to Spring's claim of priority (this vol., ii, 275), the author maintains that neither Spring nor anyone else had shown the carrying through of a truly endothermic reaction (that is, one requiring the continual supply of energy during the whole reaction, and not only for the starting of the reaction) by purely mechanical means, and so maintains his own claim to priority. L. T. T.

**Endothermic Reactions effected by Mechanical Force.** By W. SPRING (*Zeit. anorg. Chem.*, 7, 51).—A reply to M. C. Lea (see preceding abstract), maintaining his former claim. L. T. T.

**Apparatus for Facilitating the Boiling of Liquids.** By V. GERNHARDT (*Ber.*, 27, 2640—2641; compare this vol., ii, 268).—The apparatus in question is identical with Beckmann's (*D.R.P.* 53,217). M. O. F.

**Apparatus for Continuous Evolution of Gas.** By N. TECLU (*Zeit. anal. Chem.*, 35, 441—446).—This is a modification of Ostwald's hydrogen sulphide apparatus (*Abstr.*, 1893, 268). M. J. S.

**Improved Drying Oven.** By W. HOFFMEISTER (*Zeit. anal. Chem.*, 35, 437—438).—The oven is designed for drying substances in a current of illuminating or other gas, or under reduced pressure.

The form is that of the ordinary rectangular chest, but the door is made to close air-tight. The gas with which it is to be filled is introduced by a copper spiral pierced with numerous holes. Openings at the top of the chest allow of the insertion of a thermometer and a tube, by which connection may be made either with the burner which is to consume the gas after passing through the oven, or with a pump, by which, when the inlet tube is closed, the pressure in the interior may be lowered.

M. J. S.

## Inorganic Chemistry.

**Preparation of Chlorine for Laboratory Purposes.** By F. A. GOOCH and D. A. KREIDER (*Zeit. anorg. Chem.*, 7, 17—21).—When hydrochloric acid of sp. gr. 1.1, heated to about 80°, is allowed to come slowly in contact with pieces of potassium chlorate which have been previously fused, a steady evolution of gas takes place. Under these conditions, about 82—85 per cent. of the gas is chlorine, the remainder being chlorine dioxide. Another 10 per cent. of the dioxide may be decomposed by passing the evolved gas through a saturated hydrochloric acid solution of manganous chloride at 90°. If the gas is wanted absolutely pure, the gas, after passing through the manganous chloride, may be passed through a combustion tube filled with asbestos and heated to redness. Care must be taken to have the acid hot, and not to allow the action to become rapid, or the proportion of chlorine dioxide may become much increased and explosion occur. 1 gram of potassium chlorate yields about half a litre of chlorine.

If a Kipp or some similar constant gas generating apparatus is employed, and the acid heated by a steam jacket or by standing the generator in hot water, this method forms a convenient constant chlorine apparatus for laboratory use.

L. T. T.

**The Condition of Iodine in Solution, and the probable Cause of the different Colours of its Solutions.** By G. KAÜSS and E. THIELE (*Zeit. anorg. Chem.*, 7, 52—81; compare Gautier and Charpy, *Abstr.*, 1890, 446).—The authors detail numerous determinations of the molecular weight of iodine in solution, and also of its absorption spectra in 34 solvents (in each case at two temperatures).

Although the boiling and freezing point experiments negative the existence of complex chemical molecules of iodine, the authors believe that they do not disprove the possibility of complex "physical molecules" or groups of molecules. The experiments of Anschütz, Behrend, and others on the freezing points of solutions of naphthalene and picric acid in benzene and chloroform, of phenanthrene picrate in alcohol, &c. (where figures are obtained such as would be expected

if the molecule had become dissociated whilst other evidence is against such dissociation), points to the possibility of the existence of such loosely bound groups of molecules without their being detected by the Raoult method. Determinations of the molecular weight of anthracene picrate in benzene made by the authors, both by the boiling point and freezing point methods, gave half the true molecular weight, or results such as would be expected if dissociation had occurred, whilst the dark red colour of the solution showed that such dissociation had not taken place.

The behaviour of iodine in its compounds also points to a tendency to form molecular aggregates. Thus the polyiodides all contain  $I_2$ , or a multiple thereof, and never an uneven number of iodine atoms in excess of those in the simple iodide.

The authors conclude that the fundamental colour is dependent on the aggregation of the molecules of the iodine. In the brown solutions, the dissociating power of the solvent is not sufficient to overcome the aggregating tendency of the iodine molecule, and the iodine is in the form of  $[I_2]_n$ , whilst in violet solutions the iodine exists in its simple form of  $I_2$ . This would also account for the fact that brown iodine solutions tend, when heated, to pass into violet, and violet solutions when much cooled to change to brown. It is probable that the refractive and dispersive powers of the solvent may also have its influence in displacing the absorption bands, and that some of the variations in shade of the solutions may be due to this cause.

L. T. T.

**Action of Reducing Agents on Iodic acid.** By Miss C. F. ROBERTS (*Amer. J. Sci.*, [3], 48, 151—158).—Most text books state that nitric oxide is absorbed by aqueous iodic acid with liberation of iodine, but of the character and degree of ease of the reaction little is known. The authoress finds that nitric oxide causes no appreciable separation of iodine from dry iodic acid, or from solutions of that acid in sulphuric acid. Nitric oxide is, however, absorbed by aqueous solutions of iodic acid of any strength, but the reaction takes place slowly even when the gas is confined over the acid, and not at all when the gas is merely passed rapidly through the solution.

When potassium iodide is added to dilute solutions of iodic acid, or of hydrochloric acid, no iodine is separated; but when a solution of potassium iodide is gradually added to a mixture of weak solutions of iodic and hydrochloric acids, the solution becomes yellow, then orange, and, finally, particles of iodine separate. The iodine could not be detected by the starch reaction, as iodine monochloride is one of the products first formed. When iodic acid is in excess, the reaction takes place according to the equation  $HIO_3 + 2KI + 5HCl = 3H_2O + 2KCl + 3ICl$ . Part of the iodine monochloride is subsequently decomposed with liberation of iodine. Other reducing agents, such as sodium thiosulphate, arsenious anhydride, ferrous sulphate, stannous chloride, potassium thiocyanate, and nitric oxide produce similar effects.

Although a solution of iodine in iodic acid turns starch blue, as does also one of iodine in hydrochloric acid, yet, if the two solutions be

mixed, the starch immediately loses its blue tint, but regains it on the addition of an alkali carbonate. The proportions in which iodic acid and iodine were found to react in presence of hydrochloric acid were as 1 : 4. The reaction takes place according to the equation  $\text{HIO}_3 + 2\text{I}_2 + 5\text{HCl} = 3\text{H}_2\text{O} + 5\text{ICl}$ .

It is probable that the action of potassium iodide or other reducing agent on iodic acid in presence of hydrochloric acid is first to liberate iodine, which at once acts on the mixture of the two acids to form iodine monochloride. It could not be ascertained whether the first action on the iodic acid was to form a higher oxide ( $\text{I}_2\text{O}_7$ ) or a lower ( $\text{I}_2\text{O}_4$ ). Whichever is the case, the mixture of iodine and iodic acid, both ordinarily oxidising agents, is able to effect the decomposition of hydrochloric acid with formation of iodine monochloride.

L. T. T.

**Ozonising Apparatus.** By H. N. WARREN (*Chem. News*, 70, 41—42).—Pieces of tinfoil, in close proximity to one another, are attached to the inner surface of glass tubes (similarly to the diamond Leyden jar), and can then be used for ozonising air or oxygen, in place of the usual apparatus.

D. A. L.

**Influence of Pressure on the Combination of Hydrogen with Selenium.** By H. PÉLABON (*Compt. rend.*, 119, 73—75).—When selenium is heated at  $620^\circ$  with hydrogen in sealed tubes in which the pressures are respectively 520 mm., 1270 mm., 1520 mm., and 30,160 mm., the values obtained for the ratio of the partial pressure of the hydrogen selenide to the total pressure are 0.405, 0.4112, 0.42, and 0.423 respectively. At  $575^\circ$ , for pressures of 678 mm. and 1380 mm., the ratios were 0.39 and 0.403 respectively. At a much lower temperature, namely,  $310^\circ$ , and pressures of 580 mm. and 1520 mm., the ratios were 0.214 and 0.23 respectively. It follows that, as Ditte has already observed, an increase of pressure increases very slightly the quantity of hydrogen selenide produced at a given temperature, and the effect of pressure is less the higher the temperature. This result is in agreement with the ordinary theory of dissociation.

The author finds that increase of pressure increases the rate of formation of the hydrogen selenide.

C. H. B.

**Action of Chlorine on Phosphonium Iodide.** By J. C. CAIN (*Chem. News*, 70, 80—81).—By the action of chlorine or phosphorus pentachloride on phosphonium iodide, a mixture of amorphous phosphorus and solid hydrogen phosphide is obtained.

D. A. L.

**Bromoborates.** By G. ROUSSEAU and H. ALLAIRE (*Compt. rend.*, 119, 71—73; compare this vol., ii, 413, and *Abstr.*, 1893, ii, 518).—The action of bromine on a mixture of a metal with boronatrocalcite yields a series of bromoborates analogous to the chloroborates previously described (*loc. cit.*). Heintz's method, which in the case of chloroborates is satisfactory only for the zinc salt, is, in the case of bromoborates, satisfactory only for the zinc and magnesium compounds.

The *bromoborates* have the general formula  $6M''O, 8B_2O_3, M''Br_2$ , and crystallise in cubes, tetrahedra, and dodecahedra, which act on polarised light, and seem to have only a pseudocubic symmetry. The magnesium, zinc, cadmium, and manganese compounds are colourless; the cobalt compound is green by transmitted light, and violet by reflected light; the nickel compound is yellow.

In all cases where the bromoborate has been prepared from boronatrocalcite, it contains about 1 per cent. of calcium.

C. H. B.

**Behaviour of Sodium Peroxide towards Alcohol.** By J. TAPPEL (*Ber.*, 27, 2297—2306; see also this vol., ii, 233).—A compound of the composition  $Na_2O_2 \cdot H$ , which the author names *sodyl-hydroxide*, is obtained when sodium peroxide is shaken with well cooled absolute alcohol. It remains undissolved as a yellowish sandy mass, whilst the alcoholic solution contains only traces of active oxygen. It dissolves in water with a much smaller development of heat than sodium peroxide, and, when heated in a tube, explodes with evolution of oxygen. It also slowly gives off oxygen at  $0^\circ$ , absorbs water from the air, and is converted by dry carbonic anhydride into sodium carbonate, water, and oxygen. It dissolves in ice-cold water without evolution of gas, but a slight rise of temperature determines decomposition; when mixed with dilute alcohol, it yields crystals of the compound  $Na_2O_2 \cdot 8H_2O$ ; with alcoholic hydrogen chloride at  $-5^\circ$ , it yields a product which contains 1 mol.  $NaCl$  and 1 mol.  $NaO_2 \cdot H$ ; at higher temperatures the products of the action are sodium chloride and hydrogen peroxide. It dissolves in cold alcoholic acetic acid, and forms a compound of the formula  $NaC_2H_3O_2 \cdot NaOC_2H_3O_2 \cdot H_2O$ . With benzoic chloride at ordinary temperatures, it yields sodium chloride and benzoic peroxide (m. p.  $105^\circ$ ).

E. C. R.

**Preparation of Ammonium Nitrite.** By S. P. L. SÖRENSEN (*Zeit. anorg. Chem.*, 7, 33—40).—The author employs a modification of Erdmann's method. The mixture of nitrogen oxides evolved during the action of arsenious anhydride on nitric acid is passed over coarsely powdered ammonium carbonate kept cool by ice. The half liquid mass is treated with alcohol, the unchanged carbonate filtered off, and the ammonium nitrite precipitated by the addition of ether. The nitrite so obtained is of 90—94 per cent. purity, and may be purified by re-solution in 96 per cent. alcohol and reprecipitation with ether.

Pure ammonium nitrite forms almost colourless needles which are deliquescent, and dissolve in water with development of heat. It is easily but slowly soluble in alcohol, and is precipitated from this solution by ether, chloroform, and ethylic acetate. Concentrated solutions appear to decompose with explosive force at  $60$ — $70^\circ$ , like the solid salt, and in acid solutions such decomposition sometimes occurs at ordinary temperatures. The dry salt may be safely kept in an atmosphere of hydrogen, and in presence of pieces of ammonium carbonate and of lime. It is best kept and transported under absolutely dry and alcohol-free ether.

L. T. T.

**Preparation of Potassium Mercuric Iodide.** By E. G. CLAYTON (*Chem. News*, 70, 102).—Potassium mercuric iodide is readily obtained from ordinary Nessler solution by concentration and crystallisation. D. A. L.

**Molecular Weight of Mercurous Chloride.** By M. FLEHII (*J. pr. Chem.*, [2], 50, 222—223).—A propos of the paper of Harris and V. Meyer on this subject (this vol., ii, 353), the author calls attention to the fact that, already in 1881, he had determined the vapour density of mercurous chloride, by V. Meyer's method, in an atmosphere of mercuric chloride, and found it to correspond with  $\text{HgCl}$  (*Gazzetta*, 11, 341). That no dissociation had taken place was proved by the fact that a cooled gold surface, immersed in the mixed vapours at  $400^\circ$ , received no deposit of mercury. C. F. B.

**Separation of the Rare Earths.** By H. A. ROWLAND (*Chem. News*, 70, 68—69).—The author, like other investigators, finds cerium, lanthanum, praseodymium, neodymium, and thorium differ from the yttrium group, and confirms the occurrence of all these earths, in varying proportions, in such minerals as gadolinite, samarskite, yttrialite, cerite, &c., but adds, that besides the elements of the cerium group, there are at least seven other substances, which he refers to as *a*, *b*, *i*, *d*, *h*, *u*, *c*, *k*. These are separated from the cerium group by fractionating with sodium sulphate. The mixed earths are dissolved in a slight excess of nitric acid, the solution diluted and kept warm while solid sodium sulphate is stirred in, during a day or two, until the absorption lines of neodymium, the most persistent of the group, disappears from the solution. The precipitate is treated with potash, and the resulting oxides submitted to the same course of treatment, which is repeated a dozen times. The substances *a*, *b*, *d*, *i* appear in the early solutions; *d*, *u*, *c*, &c., in the later ones, and can be obtained fairly free from *a*, *b*, and *i*; but *d* persists throughout, even in the precipitate of the cerium group. Samarskite, as compared with gadolinite, not only contains more of the mixture *d*, *u*, &c., but also a larger number of elements, one of them being the author's *h*. The sulphates of sodium and potassium each exhibit varying degrees of activity towards these different substances, moreover, the oxalates differ in solubility, but not sufficiently to permit of effective separation. The author has separated *a* from the others in the following manner:—The solution from the sulphate fractionation is slightly acidified with nitric acid, diluted, and treated with weak potassium ferrocyanide solution, at intervals of an hour or so, until cerium bands are no longer visible from 3 inches of the strong solution. The earth is then precipitated as oxalate, and may be obtained quite pure by this method, which, however, only serves for the isolation of *a*. *a* is the principal element of, and has the properties of yttrium, and both the oxalate and oxide are white.

The mixture of *b*, *i*, *d* gives cerium absorption and emission bands, but of the former many seem to belong to *b* rather than to *i*. The oxalate of this mixture is red, and the oxide white. *b* is strong in

gadolinite and weak in samarskite. The spectrum of the author's erbium indicates the presence of a fourth constituent.

Substance *d* has not been isolated, but has, nevertheless, been named demonium, on account of its ubiquity and persistency; *a* is the only one of these substances obtained free from it. The principal spectrum line of *d* is at wave-length 4000.6 nearly. The substances *u*, *k*, *c* have a feeble absorption spectrum in the visible spectrum, and a strong one in the ultra violet. Of *h*, no properties have been ascertained.

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**Separation of the Rare Earths.** By W. CROOKES (*Chem. News*, 70, 81—82).—It is pointed out that Rowland's substances, *a*, *b*, *i*, &c. (preceding abstract), are probably already known by accepted names; that white yttrium oxalate and oxide are far from novelties, and that the erbium known to chemists generally, retains its white oxalate, its rose oxide, and a number of bands in its absorption spectrum even after its various acknowledged constituents have been separated.

D. A. L.

**Impurities in Aluminium.** By H. MOISSAN (*Compt. rend.*, 119, 12—15).—The usual impurities in commercial aluminium are iron, derived from the raw materials and from the electrodes, and silicon, derived partly from the electrodes and the crucible, but chiefly from the alumina. There is no evidence, in many cases, that silicon has any injurious effect, but it can be partially removed by melting the metal under a layer of an alkali fluoride. In addition to these two impurities, aluminium contains a small quantity of nitrogen, which is evolved as ammonia when the metal is dissolved in potassium hydroxide, and a small quantity of carbon, which remains as a maroon coloured, amorphous residue, quite free from graphite, when the metal is heated with gaseous hydrogen chloride or hydrogen iodide free from oxygen and the greyish residue is treated with dilute hydrochloric acid. The nitrogen is probably present in the form of aluminium nitride; it slightly reduces the breaking strain, the elongation, and the limit of elasticity. The carbon has a much more marked effect in reducing both the breaking strain and the elongation.

Commercial aluminium also contains a small quantity of amorphous alumina, and sometimes small crystals of carbon boride.

C. H. B.

**Aluminium Carbide.** By H. MOISSAN (*Compt. rend.*, 119, 16—20).—Aluminium carbide,  $C_3Al_4$ , is obtained (1) by heating aluminium in carbon dishes, in the electrical tube-furnace, with a current of 300 ampères and 65 volts, a current of hydrogen being passed through the tube; (2) by heating the metal in a carbon crucible in the electrical furnace, the product in this case being contaminated with nitrogen; or (3) by reducing a mixture of kaolin and carbon in the electrical furnace. In order to remove the excess of metal, the product is treated with concentrated hydrochloric acid at a low temperature, washed rapidly with water, and finally with alcohol.

Aluminium carbide forms transparent, yellow crystals, sometimes 5—6 mm. long; sp. gr. = 2.36. Some have the form of regular hexagons. It is decomposed at the highest temperatures of the electric arc; chlorine attacks it at a dull red heat, with incandescence, aluminium chloride volatilising, and a residue of amorphous carbon, without any trace of graphite, being left; bromine has no action at the ordinary temperature, but attacks the carbide, with incandescence, at about 700°; iodine seems to have no action, even at a bright red heat. Oxygen attacks the carbide superficially only at a dull red heat, whereas at the same temperature sulphur attacks it readily, with great development of heat, and formation of aluminium sulphide and traces of carbon bisulphide, although the greater part of the carbon remains in the form of thin lamellæ. Nitrogen and phosphorus have no action on the carbide at a dull red heat, but certain oxidising agents attack it readily. When slightly heated with dry potassium permanganate, it is oxidised with vivid incandescence; potassium dichromate and chromic anhydride oxidise it slowly at dull redness.

The carbide reduces lead peroxide and the red oxide with incandescence, but it is not attacked by potassium chlorate or nitrate. A solution of an alkali dichromate acidified with sulphuric acid attacks it slowly in the cold, or when boiled; fuming nitric acid is without action, even on heating, but on the addition of water the carbide is rapidly attacked; concentrated hydrochloric acid attacks it very slowly, but the dilute acid dissolves it in a few hours; boiling concentrated sulphuric acid is reduced, with formation of sulphurous anhydride, and the dilute acid reacts at about 100°. Fused potassium hydroxide attacks the carbide with great energy at about 300°, but alkali carbonates, even at a bright red heat, produce only incomplete decomposition.

When the carbide remains in contact with water at the ordinary temperature, decomposition takes place very slowly, with liberation of methane and formation of aluminium hydroxide, the change being accelerated by heat, but not appreciably influenced by light.

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**Behaviour of Various kinds of Glass with Reagents.** By F. FOERSTER (*Zeit. anal. Chem.*, 35, 381—396).—Out of 14 varieties of glass, all of high repute for chemical purposes, the borosilicate Jena glass, 59 III, and the hard zinc-aluminium-sodium glass (Jena, 165 III) are much less attacked by water at 20° or 80° than any of the others. The borosilicate glass, and glasses containing zinc, are more strongly attacked by sodium hydroxide than those containing aluminium. The glasses least attacked by water at 190° are those whose composition approaches nearest to the normal formula,  $6\text{SiO}_2 \cdot \text{R}'\text{O} \cdot \text{R}''\text{O}$ , when R' is calcium or zinc, but the glass least affected as regards amount of alkali dissolved, although in respect of total substance dissolved it is surpassed by Stas's calcium-potassium-sodium glass, is the Jena, 59 III, which, moreover, has the great advantage of retaining its transparency, an important point in the selection of a glass for the water-level gauges of boilers.

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M. J. S.

**Cementation Steel, Ferrochromium, Ferrotungsten, Chromium Steel, Tungsten Steel.** By H. BEHRENS and A. R. VAN LINDE (*Rec. Trav. Chim.*, 13, 155—181).—The specimen of cementation steel was prepared from puddled Dannemora iron; it readily fractured, and the surface was studded with glittering spangles. When polished and etched, the metal shows the presence of disseminated hard particles; these resemble white cast iron, and were isolated by dissolving the metal in acid. This substance constitutes about 5 per cent. of the steel, its hardness is slightly greater than 5; it is extremely brittle, and contains 66 per cent. of carbon, corresponding with the formula  $\text{Fe}_3\text{C}$ . The original steel contained 0.74 per cent. of carbon, and 0.02 per cent. of phosphorus, consequently, when freed from the carbide, it only contained 0.4 per cent. of carbon. A detailed description is given of the microscopic appearance of the steel as it gradually dissolved in acids, the portions presenting the greatest resistance to corrosion being distributed irregularly throughout the bar; this accords with Laurent's theory, that during cementation the steel derives its carbon from carbonic oxide.

Ferrotungsten, when etched, shows the presence of hard, almost rectangular, crystals. Two alloys can be distinguished, the one is white, the other grey; the hardness = 6—6.3 and 4.2—4.5 respectively. After treatment with acid, light coloured crystals separate; their hardness is between that of felspar and quartz; they are attracted by an electro-magnet, but not by a permanent one; they contain 0.56—0.62 per cent. of carbon, and probably have the formula  $\text{Fe}_3\text{W}$ . Ferrotungsten appears to resemble ferroaluminium. Attempts to isolate the compound to which tungsten steel owes its extreme hardness were unsuccessful.

Ferrochromium also contains crystals, the hardness of which = 6, whilst that of the magma = 4.2; the latter is a much better conductor of heat than the former. Treatment with acid leaves bayonet-shaped crystals, which are not magnetic; their hardness = 7.5. In ferrochromium with 13.3 per cent. of chromium, and 5.5 per cent. of carbon, the composition of these crystals corresponds with the formula  $\text{Cr}_3\text{Fe}_2\text{C}_3$ , corresponding with the ferrocabide,  $\text{Fe}_3\text{C}$ ; in ferrochromium with 50 per cent. of chromium, the composition is approximately  $\text{Cr}_2\text{FeC}_2$ . It is pointed out that the softer portions of the alloy contain considerable quantities of chromium, and consequently, as Hadfield has shown, the hardness is very closely connected with the quantity of carbon present; probably the action of chromium is twofold; it forms double carbides, less soluble in molten iron than the ferrocabides, and at the same time facilitates the crystallisation of the latter. The crystals from chrome steel are smaller than those from ferrochromium, but in composition and properties closely resemble those from ferrochromium containing 13 per cent. Cr.

The paper concludes with a discussion and condemnation of the theory of the existence in various alloys of allotropic forms of the metals. Full analytical details are given, as also diagrams of some of the crystals. J. B. T.

**Chromium.** By H. MOISSAN (*Compt. rend.*, 119, 185—191).—By means of the electric furnaces previously described (Abstr., 1893,

ii, 281, and this vol., ii, 78). the author has prepared more than 20 kilos. of metallic chromium.

*Chromium Carbides*.—When chromium is heated with a large excess of carbon in the crucible of the electric furnace with a current of 70 volts and 350 ampères for 10 or 15 minutes, the carbide,  $\text{C}_2\text{Cr}_3$ , is obtained in very brilliant lamellæ with a greasy lustre: sp. gr. = 5.62. The crystals are not attacked by concentrated or dilute nitric acid, aqua regia, or concentrated hydrochloric acid, but they are slowly decomposed by dilute hydrochloric acid. Fused potassium hydroxide has very little action on the carbide, but fused potassium nitrate attacks it readily. It is not decomposed by water even at  $100^\circ$ . It is much harder than quartz, and is even harder than topaz, but is softer than corundum.

Another carbide,  $\text{CCr}_4$ , is obtained in lustrous needles, sometimes 10—20 mm. long on the surface of the ingots of metallic chromium or in the cavities formed in the interior of the ingots; sp. gr. = 6.75. It is much harder than glass, and somewhat harder than quartz.

*Chromium*.—When the crude chromium is heated with excess of chromium oxide with a view to remove the carbon, the resulting metal is partially oxidised or “burnt.” By heating the chromium in the electric furnace with calcium oxide, the greater part of the carbon is removed as calcium carbide, and the metal contains only 1.5—1.9 per cent. of carbon. When thus purified, it crystallises very readily, and the crystals, which often are 3—4 mm. long, seem to be cubes and octahedra, and resemble bismuth crystals in their grouping.

The complete removal of carbon from chromium by means of calcium oxide is not possible, because when the proportion of carbon has been reduced below a certain point, an inverse action takes place with formation of a well crystallised chromium calcium oxide. If, however, the chromium is heated in an electric furnace made of lime and brasqued with this double oxide, metallic chromium is obtained quite free from carbon; sp. gr. at  $20^\circ$  = 6.92.

When chromium containing 2 per cent. of carbon is heated before the oxyhydrogen blowpipe, it partially burns, with production of brilliant sparks, and the heat developed by this combustion causes the superficial fusion of the metal at the point on which the flame impinges, but the metal could not be fused in an ordinary platinum furnace even after heating for 45 minutes. Pure chromium burns in the oxyhydrogen blowpipe more brilliantly than iron, and can be completely oxidised. It is less fusible than the metal containing carbon, and its melting point is considerably higher than that of platinum, and cannot be obtained by means of the oxyhydrogen flame. In the electric furnace, however, it melts to a brilliant, very mobile liquid, and by means of a current of 70 volts and 1000 ampères, as much as 10 kilos. of chromium can be melted at once and cast into ingots.

Pure chromium is somewhat harder than glass, but not so hard as quartz; it can be worked with a file, and takes a polish similar to that of iron, but more brilliant and somewhat whiter. Chromium containing 1.5—3.0 per cent. of carbon can only be cut and polished

with a wheel armed with diamonds. The pure metal is not magnetic.

Crude chromium does not alter when exposed to moist air, but the pure metal oxidises superficially only, and afterwards undergoes no further change. It burns brilliantly in oxygen at  $2000^{\circ}$ , and burns in sulphur vapour at about  $700^{\circ}$  with formation of chromium sulphide. When heated with carbon at the temperature of a forge, it forms the carbide  $\text{CCr}_2$ , and, at the temperature of the electric furnace, the carbide  $\text{C}_2\text{Cr}_3$ . In the electric furnace, it combines readily with silicon, forming a crystallised silicide which easily scratches rubies, and is not attacked by acids, aqua regia, or fused potassium hydroxide or potassium nitrate. Under similar conditions, it forms a well crystallised boride which is very hard, and is attacked by acid with difficulty.

When heated to dull redness in hydrogen chloride, chromium is readily attacked, and yields crystallised chromous chloride. Hydrochloric acid attacks the metal very slowly in the cold, and more rapidly on heating. Under the influence of an electric current, the metal being the positive pole, it will dissolve in the dilute acid. Boiling concentrated sulphuric acid attacks chromium with evolution of sulphurous anhydride and formation of a deep coloured solution; the hot dilute acid attacks it slowly, and out of contact with air forms the blue, crystalline chromous sulphate previously described. Cold or hot fuming nitric acid or aqua regia has no action on chromium; dilute nitric acid attacks it very slowly. Mercuric chloride solution attacks the powdered metal very slowly with formation of chromic chloride.

When heated at  $1200^{\circ}$  in a current of hydrogen sulphide, chromium is completely converted into fused chromium sulphide, which has a crystalline appearance; at the same temperature, carbonic anhydride attacks the metal with formation of a superficial layer of green chromic oxide mixed with carbon, whilst carbonic oxide yields chromic oxide and carburated chromium.

Fused potassium nitrate readily attacks chromium at a dull red heat, but the action is still more vigorous with fused potassium chlorate, on the surface of which the burning chromium floats in the same way as potassium on water. Fused potassium hydroxide, on the other hand, has no appreciable action on chromium at a dull red heat.

C. H. B.

**Phosphorus Pentachloride and Molybdic Anhydride.** By H. SCHIFF (*Zeit. anorg. Chem.*, 7, 91).—A reply to Smith and Sargent (*Zeit. anorg. Chem.*, 6, 384).

**Action of Molybdenum Dioxide on Silver Salts.** By E. F. SMITH and O. L. SHINN (*Zeit. anorg. Chem.*, 7, 47—49).—The authors find that molybdenum dioxide is readily dissolved by a slightly warm aqueous solution of silver nitrate, the solution being rendered more rapid by the presence of ammonia. Silver at the same time separates out in crystalline scales.

L. T. T.

**Action of Molybdic acid on Potassium Chromate and Dichromate.** By R. H. BRADBURY (*Zeit. anorg. Chem.*, 7, 43—46).—When molybdic acid is dissolved in a solution of potassium chromate, and the mixture evaporated to a small bulk, most of the acid separates unchanged; a small quantity of potassium molybdate is, however, formed, and a corresponding quantity of potassium dichromate. When molybdic acid is dissolved in potassium dichromate solution and the solution evaporated, no action appears to take place. When dry molybdic acid is mixed with dry potassium dichromate and gently fused in a crucible, a brownish powder is formed, which is insoluble in water, soluble to a green liquid in hydrochloric acid, and has the formula  $K_2O, Cr_2O_3, 3MoO_3$ .

L. T. T.

**Action of Hydrogen Chloride on Sodium Vanadate.** By E. F. SMITH and J. G. HIBBS (*Zeit. anorg. Chem.*, 7, 41—42).—Debray has shown that molybdic acid can be volatilised in a current of hydrogen chloride. The authors find that when a current of hydrogen chloride is passed over sodium vanadate, heated at  $440^\circ$ , the whole of the vanadic acid is volatilised, sodium chloride being left. The volatile product condensed on the cool part of the tube as a semi-opaque, reddish-brown, oily liquid, which is probably the compound  $2VO_2, 3H_2O, 4HCl$ , described by Berzelius.

L. T. T.

**Niobium and Tantalum.** By E. F. SMITH and P. MAAS (*Zeit. anorg. Chem.*, 7, 96—99).—Niobium oxide when heated strongly in a stream of hydrogen chloride yields a white sublimate of the formula  $Nb_2O_5, 3H_2O, HCl$ , which the author considers to be a *hydrorychloride*. It is volatile at very high temperatures. Hydrogen bromide yields a similar *hydrorybromide*, which is yellowish-red, and rather more easily volatile than the chlorinated compound. This volatility of niobium oxide in halogen acids, although much less marked than that of molybdic acid, may give a means of removing traces of niobium from tungsten and other non-volatile substances. Tantalum oxide, under like conditions, is unchanged.

When niobium oxide is fused with a large excess of metallic magnesium, a blue-black *oxide*,  $Nb_2O_4$ , is produced. It is insoluble in all acids except hydrofluoric, and, when heated in the air, is converted into white niobium oxide. When tantalum oxide is heated with metallic magnesium, a strong action occurs, and a brownish-black *tetroxide*,  $Ta_2O_4$ , is produced; this is not attacked by hydrochloric, nitric, or sulphuric acid. When heated with chlorine, this oxide gives a white, easily volatile sublimate, which is readily decomposed by water, and contains 18.5 per cent. of chlorine. When tantalum oxide is heated with aluminium powder, violent action takes place, the whole mass becoming red hot; the above-mentioned tetroxide seems to be formed, but was never obtained free from aluminium.

L. T. T.

**Haloid Compounds of Platinum.** By L. PIGEON (*Ann. Chim. Phys.*, [7], 2, 433—502; compare Abstr., 1890, 439; 1891, 900, 1325; 1892, 3).—In addition to the tetra- and penta-hydrates of platinum chloride, the author has prepared two others. The *hepta-*

*hydrate*,  $\text{PtCl}_4 \cdot 7\text{H}_2\text{O}$ , is obtained on allowing neutral platonic chloride solution to evaporate in a vacuum; on exposure to a dry atmosphere, it effloresces, leaving the tetrahydrate. The monhydrate is formed on exposing the latter over potash in a vacuum at  $100^\circ$ .

Although the action of chlorine on platinum is not complete, yet on passing chlorine through arsenic chloride containing spongy platinum mixed with rather less than its weight of selenium, the whole dissolves. After heating the solution in a sealed tube at  $250^\circ$ , a yellow, crystalline double compound of platonic and selenic chlorides is deposited; this, on heating at  $360^\circ$  in a current of chlorine, yields nearly pure platonic chloride. If platinum selenide is used instead of a mixture of its constituents, no action occurs. The above double compound is fairly soluble in boiling arsenic chloride, whilst platonic chloride is very sparingly so.

Platonic iodide,  $\text{PtI}_4$ , separates on adding potassic iodide to hydrogen platinochloride solution. On heating it in a current of chlorine, platonic chloride is obtained; the product nearly always contains traces of iodide.

Dry platonic iodide decomposes slowly with evolution of iodine in a vacuum at ordinary temperatures. The heat of formation of the iodide was determined.

$\text{Pt solid} + \text{I}_2 \text{ solid} = \text{PtI}_4 \text{ solid, develops } 17.4 \text{ Cals.}$

$\text{Pt solid} + \text{I}_2 \text{ gaseous} = \text{PtI}_4 \text{ solid, develops } 39.0 \text{ Cals.}$

W. J. P.

## Mineralogical Chemistry.

**Separation of Minerals of High Specific Gravity.** By S. L. PENNIE and D. A. KRAMER (*Amer. J. Sci.*, [3], 48, 143—144).—The authors point out the value to mineralogists of the discovery by J. W. Retgers (*Abstr.*, 1893, ii, 294) of the possibility of using the fused double nitrate of silver and thallium (sp. gr. = 5) for separating minerals. The liquid has the advantage of being practically colourless, neutral, soluble in water, and readily recoverable from the aqueous solution by simple evaporation on the water bath. Separations may be made in test tubes. Some disadvantages are, however, presented, and these are obviated in an apparatus, devised by the author, of which illustration, are given.

B. H. B.

**Nitrogen Content of Californian Bitumen.** By S. F. PECKHAM (*Amer. J. Sci.*, [3], 48, 250—255).—The author found that the oils from the tunnels in Wheeler's Cañon on the south side of the Sulphur Mountain, Ventura Co., California, yielded the following results on analysis—

H.	C.	N.	Total.
11.82	86.93	1.11	99.86

The oil of the Pico Spring contained 1.02 per cent. of nitrogen, and that from the Cañada Laga Spring 1.08 per cent.

By washing a distillate of California petroleum with dilute sulphuric acid, basic oil is obtained, demonstrating the animal origin of the bitumens. The author has tested all of the varieties of bitumen found in California, from the most fluid petroleums to solid asphaltum, and has invariably observed the reaction indicating the presence of these compounds.

B. H. B.

**Natural Occurrence of Humic acid.** By C. v. JOHN (*Zeit. Kryst. Min.*, 23, 289; from *Verk. k. k. Geol. Reichsanst.*, 1891, 64).—At the outcrop of a coal seam at Theussau, near Falkenau, in Bohemia, a carbonaceous mass was met with which was completely soluble in ammonia and sodium carbonate, and was reprecipitated on the addition of hydrochloric acid. At 100° 59.25 of water was given off, the residue consisting of—

C.	H.	O.	Ash.
54.48	4.64	39.98	0.40

The formula was thus  $C_{48}H_{48}O_{25}$ .

B. H. B.

**Rumänite.** By O. HELM (*Zeit. Kryst. Min.*, 23, 308—309; from *Schriften d. naturf. Gesell. zu Danzig*, 7, No. 4).—At several places in Roumania an amber-like fossil resin occurs, to which the author gives the name of *rumänite*. It is of a brownish-yellow colour, transparent to translucent, much fissured, and brittle. It has a conchoidal fracture, a hardness of  $2\frac{1}{2}$  to 3, and a sp. gr. of 1.048 to 1.105. Its composition is as follows.

C.	H.	O.	S.	Total.
81.64	9.65	7.56	1.15	100.00

B. H. B.

**Dopplerite from Karkarala.** By J. A. ANTIPOFF (*Zeit. Kryst. Min.*, 23, 275; from *Trans. Russ. Imp. Min. Soc.*, 28, 503—504).—This mineral gave on analysis the following results.

C.	H.	O.	S.	Ash.
55.36	6.50	34.62	0.52	2.80

Its sp. gr. is 1.13. The volatile constituents amounted to 90.20 per cent. On heating to 100°, 2.31 per cent. was volatilised. The mineral occurs in the form of a thick and extensive deposit near the Alagn salt lake.

B. H. B.

**Jamesonite and Plumbocuprite from Semipalatinsk.** By J. A. ANTIPOFF (*Zeit. Kryst. Min.*, 23, 275—276; from *Trans. Russ. Imp. Min. Soc.*, 28, 527).—Analysis of jamesonite (I) and of plumbocuprite (II), from the Derwis Mine, in the province of Semipalatinsk, gave the following results.

	Cu.	Fe.	Pb.	Ag.	Sb.	S.	SiO <sub>2</sub>	Total.
I.	—	—	63.61	—	23.44	12.54	—	99.59
II.	69.42	0.71	9.58	0.07	trace	18.95	0.42	99.15

B. H. B.



**Argyrodite and a New Sulphostannate of Silver from Bolivia.** By S. L. PENFIELD (*Zeit. Kryst. Min.*, 23, 240—248).—A specimen from La Paz, Bolivia, which was supposed to be argyrodite, gave, on analysis, the following results.

S.	Sn.	Ge.	Ag.	Zn + Fe.	Total.
16.22	6.94	1.82	74.10	0.21	99.29

In this compound, tin is, undoubtedly, isomorphous with germanium. The formula is  $\text{Ag}_3(\text{SnGe})\text{S}_4$  or  $\frac{1}{2}\text{Ag}_3\text{S}_2(\text{SnGe})\text{S}_2$ . The only sulphostannates hitherto known to occur in nature are the rare species *stannite*,  $\text{Cu}_2\text{S}, \text{FeS}, \text{SnS}_2$ ; *frankelite*,  $5\text{PbS}, \text{Sb}_2\text{S}_3, 2\text{SnS}_2$ ; and *plumbostannite*, a mineral of doubtful composition. As the Freiberg argyrodite has been shown to be isometric, and as the name canfieldite cannot, therefore, be applied to the germanium compound, it is proposed now to transfer the name to the isomorphous tin compound.

B. H. B.

**Identity of Hydrofranklinite and Chalcophanite.** By S. L. PENFIELD and D. A. KREIDER (*Amer. J. Sci.*, [3], 48, 141—143).—The name of hydrofranklinite was given by W. T. Roepper to a supposed new hydrous oxide of iron, zinc, and manganese from Stirling Hill, New Jersey. The original chemical examination was never completed, and a new analysis has given the following results.

$\text{FeO}$ .	$\text{ZnO}$ .	$\text{MnO}$ .	O.	$\text{H}_2\text{O}$ .	Insol.	Total.
10.00	18.25	45.27	11.21	11.65	0.25	99.83

The composition of the mineral can be expressed by the formula  $\text{BMn}_2\text{O}_5, 2\text{H}_2\text{O}$ , a formula identical with that derived by Moore in 1875 for chalcophanite.

B. H. B.

**Leadhillite in Missouri.** By L. V. PIRSSON and H. L. WELLS (*Amer. J. Sci.*, [3], 48, 219—226).—The rare hydrated sulphato-carbonate of lead has been reported from but three localities in the United States. A new occurrence is now announced, near Granby, Missouri. The crystals are hexagonal prisms terminated by the base, the colour varying from colourless to clear sea-green. Analysis yielded the following results.

$\text{SO}_3$ .	$\text{CO}_2$ .	$\text{PbO}$ .	$\text{H}_2\text{O}$ .	Total.
7.33	5.14	82.44	1.66	99.59

The formula is thus  $\text{PbSO}_4, 2\text{PbCO}_3, \text{Pb}(\text{OH})_2$ , corresponding with the composition suggested by Groth.

B. H. B.

**Alunite from Colorado.** By E. B. HUELBERT (*Amer. J. Sci.*, [3], 48, 130—131).—The alunite described occurs as an aggregate of minute crystals filling pockets in the ore-body of the National Belle Mine, Red Mountain, Ouray Co., Colorado. On analysis, the mineral yielded

$\text{SO}_3$ .	$\text{Al}_2\text{O}_3$ .	$\text{K}_2\text{O}$ .	$\text{Na}_2\text{O}$ .	$\text{H}_2\text{O}$ .	Insol.	Total.
36.63	39.03	4.26	4.41	13.35	0.50	100.48

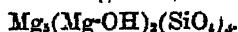
The results agree satisfactorily with the commonly accepted formula  $\text{KAl}_2\text{S}_2\text{O}_{11} \cdot 3\text{H}_2\text{O}$ . An interesting feature is, however, the large percentage of soda, alunite having usually been regarded as a potash compound only. Another interesting feature is the insolubility of the mineral in hydrochloric acid. B. H. B.

**Magnetostibian, a New Antimony Mineral.** By L. J. ILLSTRÖM (*Zeit. Krypt. Min.*, 23, 212—214).—In appearance, this mineral, which was found at the Sjö mine, resembles magnetite and jacobsite. It differs, however, from them in being transparent with blood-red colour under the microscope. It occurs in the form of grains in limestone. After the impurities had been removed, the magnetostibian gave, on analysis, the following results.

$\text{Sb}_2\text{O}_3$	$\text{As}_2\text{O}_3$	$\text{FeO}$	$\text{MnO}$	$\text{Fe}_2\text{O}_3$
9.83	1.54	17.16	59.11	12.36

The formula may be expressed thus  $(\text{MnO}, \text{FeO})_{59.11} \cdot \text{Sb}_2\text{O}_3$ . The name of magnetostibian has been selected for this mineral to indicate its magnetic properties, its similarity to magnetite and its percentage of antimony. B. H. B.

**Humite free from Fluorine.** By P. JANNACH and J. LUCKE (*Zeit. anorg. Chem.*, 7, 92—95).—Schäfer found in serpentine from the Allalinhorn, Switzerland, two minerals, one brownish-yellow and monoclinic, the other colourless, which from their optical characters are evidently humites. Both were free from fluorine. The brown mineral gave analytical results agreeing with the formula



The colourless mineral could not be obtained quite free from impurity, but appears to have the formula  $\text{Mg}_3(\text{Mg-OH})_2\text{Si}_4\text{O}_{15}$ . L. T. T.

**Constitution of the Zeolites.** By F. W. CLARKE (*Amer. J. Sci.*, [3], 48, 187—193).—The obvious relationship of many zeolites to the feldspars has long been recognised as a probable key to their constitution, but hitherto no systematic theory of the connection between the two groups has been put forward. This has now been developed by the author, and a preliminary statement of the conclusions reached is given. The complex aluminous silicates are regarded as generally being substitution derivatives of simple normal salts, and the acid radicles  $\text{SiO}_4$  and  $\text{Si}_3\text{O}_8$  are regarded as being mutually replaceable. From the albite and anorthite formulæ given by the author, those of many zeolites are easily derived, providing that the assumption is made that the soda salt may be replaced by its equivalent ortho-compound, and the calcium salt by the corresponding trisilicate. All water in the zeolites being regarded as water of crystallisation, and the groups  $\text{SiO}_4$  and  $\text{Si}_3\text{O}_8$  being represented by the general symbol X, the greater number of the numerals under consideration easily fall into two groups, having the following generalized formula.

- I.  $\text{Al}_n\text{X}_m\text{R}_p \cdot n\text{Aq}$ , and  $\text{Al}_n\text{X}_m\text{R}_p \cdot n\text{Aq}$ .
- II.  $\text{Al}_n\text{X}_m\text{R}_p \cdot n\text{Aq}$ , and  $\text{Al}_n\text{X}_m\text{R}_p \cdot n\text{Aq}$ .

The two groups remain in this form, however, only so long as water is ignored; for when the latter is regarded as partly constitutional, several members of the first series must be transferred to the second.

B. H. B.

**Microcline and Hornblende from Durbach.** By A. SAUER (*Zeit. Kryst. Min.*, 23, 291; from *Mittheil. Grossh. bad. Geol. Landesanst.*, 2, 233).—In the normal granite of Durbach, in the north of the Black Forest, small crystals of microcline (I) occur, containing a little albite. From the Durbach mica-syenite, pure material of blackish-green hornblende (II), of sp. gr. 2.94 to 2.96 was isolated by means of Klein's solution. The analytical results were as follows.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	H <sub>2</sub> O	Total
I.	64.53	19.14	trace	—	0.44	—	12.40	2.89	0.34	99.74
II.	54.89	1.50	5.06	7.46	12.08	16.01	0.38	0.37	2.72	100.47

B. H. B.

**Analyses of Hornblende.** By A. BRUNLECHNER (*Zeit. Kryst. Min.*, 23, 292—293).—Analyses of hornblende from hornblende-eclogite from Semlach (I), from Lölling (II), and from Wölch (III), in Carinthia, gave the following results.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	CaO	MgO	Total
I.	48.80	14.45	16.77	1.14	11.26	0.43	92.85
II.	45.66	14.88	17.44	1.44	10.27	4.52	94.21
III.	47.62	11.79	17.20	0.70	14.56	0.77	92.04

B. H. B.

**Bauxite from the Vogelsberg.** By A. LIEBRICH (*Zeit. Kryst. Min.*, 23, 296).—Bauxite occurs in large quantities at the Vogelsberg as an alteration product of plagioclase-basalt. The author gives the following analyses of bauxite:—I, a crystalline variety from Grabenteich; II, an amorphous variety from the Schäferling mine near Lich; and III, an amorphous variety from the Firnewald mine.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	MgO	H <sub>2</sub> O	Total
I.	1.10	50.92	15.70	3.20	0.80	0.16	28.60	100.48
II.	2.78	50.52	13.09	3.08	1.66	trace	27.12	99.15
III.	4.92	53.10	10.62	2.80	0.62	trace	27.80	99.86

B. H. B.

**Sericite from Tetschen.** By E. HIBSCH (*Zeit. Kryst. Min.*, 23, 290; from *Jahrb. k. k. Geol. Reichsanst.*, 41, 235).—Sericite (sp. gr. 2.68), from the sericite-gneiss on the right bank of the Elbe, near Tetschen, isolated by means of potassium mercury iodide solution, gave, on analysis, the following results.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	H <sub>2</sub> O	Total
	47.97	35.95	3.13	0.55	0.25	8.58	0.54	4.53	101.50

B. H. B.

**Analysis of Garnet.** By W. MÜLLER (*Zeit. Kryst. Min.*, 23, 292; from *Zeit. Deutsch. Geol. Ges.*, 43, 730).—Garnet crystals, of a blood-red colour, from the contact-metamorphosed mica-schist of the Schneekoppe, were found to have the following composition.

$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{FeO}$	$\text{MgO}$	$\text{CaO}$
34.54	22.26	7.09	32.74	2.32	1.33

B. H. B.

**Rocks and Minerals from the Island of Rhodes.** By H. v. FOELLON (*Zcit. Kryst. Min.*, 23, 293—294; from *Sitzber. d. k. Akad. Wiss. Wien.*, 100, 144).—The author gives descriptions and analyses of felspar from the uraltic gabbro of Rhoino, and from the *dykes* of Sklipio. To the same geological horizon belong asbestos-like schists, of which three varieties are described. In conclusion, he describes an asbestos-like variety of glaucophane, in which the greater portion of the  $\text{Al}_2\text{SiO}_5$  is replaced by  $\text{Fe}_2\text{Si}_2\text{O}_7$ . For this, he proposes the name of *chrysotile*.

B. H. B.

**Nepheline-syenite of Dungannon, Ontario.** By B. J. HARRIS - TON (*Amer. J. Sci.*, [3], 48, 16—18).—A remarkable mass of nepheline-syenite has been discovered at Dungannon, Hastings Co., Ontario. The rock is coarse in texture, and individuals of nepheline (Analysis I), as much as  $2\frac{1}{2}$  feet in diameter, have been observed. Sodalite (Analysis II) was found in the form of veins, streaks, and irregular masses in the rock, and the sodalite is, in places, traversed by little veins of a white and reddish mineral, which proves to be orthoclase (Analysis III). The felspar of the nepheline syenite being entirely plagioclase, the occurrence of orthoclase as a secondary mineral in the sodalite is of special interest. The following are the analytical results.

	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{FeO}$	$\text{CaO}$	$\text{MgO}$	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$
I.	43.51	33.78	0.15	—	0.16	trace	5.40	16.94
II.	36.58	31.05	—	0.20	—	—	0.79	24.81
III.	63.00	18.93	0.59	—	0.06	0.09	12.08	3.67

	$\text{H}_2\text{O}$	$\text{SO}_4$	$\text{Cl}$	Insol.	Loss on ignition.
I.	—	—	—	—	0.40
II.	0.27	0.12	6.85	0.80	—
III.	—	—	—	—	1.00

B. H. B.

## Physiological Chemistry.

**Respiratory Exchange in Cold Blooded Animals.** By H. M. VERHOFF (*J. Physiol.*, 17, 277—292).—Observations made on frogs by the use of the Pembrey-Haldane apparatus, showed:—

The evolution of carbonic anhydride in intact frogs, on gradual warming, varies within narrow limits from  $2^\circ$  up to  $17.5^\circ$ , but above this point it increases rapidly with the temperature. On cooling, it,

as a rule, becomes nearly constant from about  $17.5^{\circ}$  to  $12.5^{\circ}$  or  $10^{\circ}$ , and then decreases uniformly with the temperature.

In curarised frogs, and frogs with their bulb injured, the discharge of carbonic anhydride increases uniformly with the temperature.

If frogs are warmed and cooled rapidly several times, the curves of carbonic anhydride evolution subsequently obtained are either perfectly uniform or show abnormally marked changes at varying temperatures. The curves do not become normal again for several days after.

The respiratory quotient of winter frogs in which the bulb has not been injured is about 0.63; that of frogs with the bulb injured about 0.45; and that of curarised frogs, and frogs subjected to rapid temperature changes about 0.5.

W. D. H.

**The Action of Different Acids on Gastric Digestion.** By M. HAHN (*Virchow's Archiv*, 137, 597—604).—Various forms of proteid were digested with the usual mixture of pepsin and hydrochloric acid. In other experiments, equivalent quantities of other acids, organic and inorganic, were substituted for the hydrochloric acid. Hydrochloric acid is the most efficient acid, then comes nitric, sulphuric, and phosphoric acids in the order named, if the albumin is in solution. If, however, fibrin is used, phosphoric acid is better than sulphuric; and, for several reasons, phosphoric acid is recommended as the best substitute for hydrochloric acid. The organic acids have much less power; tartaric, oxalic, and citric acids appear to be the best; acetic acid is very feeble. Boric acid has no action at all.

W. D. H.

**Proteolysis of Crystallised Globulin.** By R. H. CHITTENDEN and L. B. MENDEL (*J. Physiol.*, 17, 48—80).—This is an account of a renewed examination of the products of the action of pepsin hydrochloric acid. The proteid selected was crystallised globulin or vitellin from hemp seed. The paper gives an account of two digestions, one of which was continued for three, and the other for ten days. The products of the digestion were carefully separated from one another and analysed; their reactions are exhaustively described, including their specific rotatory power. In separating proteoses from peptone, the difficulties of manipulation are recognised, and, so far as is at present possible, obviated. The investigation lends, however, no support to Pekelharing's suggestion that peptone is merely a portion of unprecipitated protease; whilst it is in accordance with Kühne's view that it is a definite, well-characterised substance. Its amount increases, and that of proteose diminishes, as digestion progresses, but a digestion in which all proteose has been converted into peptone has not yet been obtained. The progressive changes from primary proteose to deutero-proteose and peptone are most prominent in the early stages of digestion; the disappearance of deutero-proteose and the formation of peptone is subsequently a very gradual process.

In the proteolytic process, at least four products of hydration and cleavage are easily recognisable, namely, proto-proteose, hetero-proteose, deutero-proteose, and peptone. The examination of the

percentage composition of these substances shows a gradual and progressive falling off of carbon as digestion progresses. But the tables given show another very noticeable feature, and that is that the percentage composition of the individual proteoses differs in the two digestions; the substance called *prvto-vitellose*, for instance, in the digestion carried on for three days, cannot be the same as that with the same name in the digestion carried on for the ten day, although both give the same reactions, specific rotation alone excepted. The authors protest that this cannot be due to analytical errors, and state that other proteids, egr albumin, for instance, give similar results. The explanation advanced is that the four substances named merely represent the main steps in the hydration process, but that there are further links in the chain mixed with these which cannot at present be separated, and which manifest the same general chemical behaviour.

W. D. H.

**Nutritive Value of Sugar.** By N. ZUNTZ (*Chem. Centr.*, 1894, i, 691—692; from *Zeit. Ver. Rub-nuck.*, 1894, 64—71).—By causing a dog to mount continuously a plane inclined at  $10^{\circ}$  to the horizon, and analysing the expired air, it is possible to calculate the amount of oxygen used per kilogram-metre of work done, and also the quantity of heat produced by the combustion in which this oxygen took part. The amount of oxygen used per kilogram-metre of work done was found to be, for a diet of *lean meat*, 0.57 c.c. (2.58 Cal.); *fat*, 0.53 c.c. (2.43 Cal.); *cane sugar*, 0.54 c.c. (2.58 Cal.). Sugar, fat, and lean meat have thus about the same power of enabling physical exertion to be sustained. The efficiency of the animal body, considered as a machine, was found to be about one-third, whereas with steam-engines only one-twentieth to one-fifth of the energy of the fuel is obtained as mechanical work.

C. F. B.

**Presence of Hydrogen and Methane in the Residual Nitrogen from Blood.** By L. DE SAINT MARTIN (*Compt. rend.*, 119, 83—85).—The residual nitrogen from the blood of an ox was found to contain hydrogen amounting to 0.41—0.64 c.c., and methane amounting to 0.66—0.69 c.c. per 1,000 c.c. of defibrinated blood.

C. H. B.

**Nucleo-albumins and Intravascular Coagulation.** By W. D. HALLIBURTON and T. G. BRODIE (*J. Physiol.*, 17, 135—173).—A large number of experiments on rabbits are recorded, and the general properties of nucleo-albumins prepared from numerous tissues and organs are given. The general conclusions drawn are the following:—

1. There are two methods of preparing nucleo-albumin from organs: (1) Wooldridge's acetic acid method, and (2) a new method, consisting in the alternate treatment of the finely-minced organ or tissue with sodium chloride and water, for details of which the reader is referred to the original paper.

2. The material obtained by both methods from the same organ is the same in (1) general proteid reactions, which closely resemble those of the globulins; (2) percentage of phosphorus; and (3) physiological action, that is, the production of intravascular coagula-

tion; death is due to cessation of respiration, primarily caused, probably, in the respiratory centre.

3. The nucleo-albumins obtainable from various organs differ in some minor points, the most important being the amount of nucleïn (as evidenced by phosphorus estimation) in combination with the proteïd.

4. The sodium carbonate used as a solvent for these substances does not produce thrombosis.

5. Protagon, the most abundant impurity in these preparations, is also not responsible for the intravascular clotting.

6. These nucleo-albumins do not accelerate the coagulation of extravascular (dilute salted) plasma, and so contrast very forcibly with fibrin-ferment. The differences between fibrin-ferment and nucleo-albumin are so striking that they are possibly different substances, each, however, capable of producing fibrin under appropriate conditions.

7. Experiments with "peptone" and leech extract confirm the hypothesis of Pekelharing that these substances hinder coagulation on account of their affinity for calcium.

8. Rabbits do not show Wouldridge's "negative phase" of coagulation, but the experiments recorded, together with those of C. J. Martin (this vol., ii, 58), lend no support to the theory of Wright and Lilienfeld that this "negative phase" is produced by the splitting off of a peptone-like substance from the nucleo-albumin.

9. Typical intravascular coagulation did not, however, always occur, and the principal sources of failure are four in number.

10. The first of these relates to idiosyncrasies in the rabbit tribe, albinos being very resistant to the action of nucleo-albumin.

11. The second is due to the keeping of the nucleo-albumin too long either in contact with the acid or with the alkali carbonate used in its preparation.

12. The third is the too rapid preparation of the material. A fresh thymus yields to sodium carbonate a nucleo-albumin which is inactive, and probably is a zymogen of the active substance. A thymus which has been allowed to decompose slightly, or in which its cellular structure has been thoroughly destroyed by grinding up with sand, if treated for a few hours with dilute acetic acid yields nucleo-albumin active in producing thrombosis.

13. The fourth is due to attempts to purify the material too thoroughly. Frequent alternate treatment with acetic acid and sodium carbonate, or with sodium chloride and water, produces not only a substance which is inactive physiologically, but also one which is chemically different from the original. The chemical change is not the same in the two cases. Repetition of the sodium chloride method of preparation causes a fall in the percentage of phosphorus, due to removal of nucleïn, and a rise in the amount of ash, of which, however, sodium chloride itself forms a constant but insignificant fraction. Repetition of the acetic acid method causes either no change in the proportion of phosphorus, or more frequently a rise due to removal of the proteïd constituent of the nucleo-albumin. These statements are illustrated by tables of analyses.

14. Solutions of nucleo-albumin destroy the blood corpuscles, especially the multinucleated white ones: this, however, is largely due to their alkalinity, and will not explain the thrombosis produced. Other leucolytic agents will not produce thrombosis, even when calcium chloride is injected as well, and the experiments performed in this direction have entirely failed to confirm Löwit's work on this question.

W. D. H.

**Proteids of Red Marrow.** By J. R. FORTNA (*J. Physiol.*, 17, 174—176).—In the thymus and lymphatic glands are large collections of non-eosinophile cells, and these yield nucleo-albumin active in producing thrombosis (see preceding abstract). In the red marrow is a collection of cells which are mostly eosinophile, the granules of which give microchemically the reaction for phosphorus introduced by Lilienfeld and Monti (Sherrington, *Proc. Roy. Soc.*, 55, 161). It was judged necessary to investigate the proteids of red marrow macrochemically. The results obtained did not show any difference from those obtained from the thymus. The principal proteid obtained is nucleo-albumin, which can be prepared by both methods (see preceding abstract). It causes intravascular clotting, and is preceded in the cells by something resembling a zymogen. In addition to this, there is a globulin coagulated by heating at 47—50°, traces of an albumin and of hæmoglobin, but proteose and peptone are absent. The estimation of phosphorus in the nucleo-albumin was not performed.

W. D. H.

**Oxalates and Muscle Rigor.** By F. S. LOCKE (*J. Physiol.*, 17, 293—295).—The exposure of frog's muscle to solutions of sodium oxalate does not prevent the occurrence of *rigor mortis*, nor altogether abolish the irritability of the tissue. From this, the conclusion is drawn, not that calcium is unnecessary in these processes, but rather that it is held by the tissue so firmly that oxalate does not remove it.

W. D. H.

**The Vitreous and Aqueous Humors.** By W. PARTZ (*Z. f. Biol.*, 31, 212—243).—The paper relates specially to the question whether the aqueous and vitreous humors of the eye contain urea, dextrose, and sarcosylactic acid or not. Urea was found in the vitreous humor (0.051 per cent.) and in the aqueous humor of the ox. Dextrose was found in both humors. The possibility that aqueous humor contains another reducing substance in addition was not investigated. The vitreous humor contains sarcosylactic acid, or, more probably, salts of the acid. The aqueous humor contains the same substance, but the quantity obtained was too small to admit of a complete analysis.

W. D. H.

**Succinic acid.** By F. BLEUMENTHAL (*Virchow's Archiv*, 137, 539—568).—The best method for the isolation of succinic acid is its extraction by means of ether containing alcohol. The purification of the product obtained by evaporating the solvent, varies under certain circumstances, treated at length in the paper. Admixtures due to putrefaction can be obviated by fractional acidifying the extracting reagent.



Succinic acid is a product of the vital activity of different micro-organisms, and can be formed by these from carbohydrates, from substances allied to carbohydrates, and from albumin. Its quantity in the last-named case is dependent on the alkalinity of the mixture.

The organs obtained in the physiologically fresh condition contain no succinic acid. When it is found in them, it is a *post-mortem* product. It is, therefore, not a metabolic product of animal cells, but of micro-organisms.

Milk, on standing for months in an acid condition, contains the acid. Bacteriological investigation of such milk reveals the presence of (among others) short, rod-like microbes, which liquefy gelatin, forming there round, sharply-limited colonies. Infection of other milk with a culture of these, leads, in a few days, to the formation of succinic acid.

W. D. H.

**Formation of Sulphuric acid in the Organism.** By E. SAL-KOWSKI (*Virchow's Archiv*, 137, 381—384).—Polemical. It is pointed out that E. Baumann, in making abstracts of the papers of the author and his assistants, has misunderstood or misinterpreted his views on the subject.

W. D. H.

**Bile Pigments.** By A. JOLLES (*Pflüger's Archiv*, 57, 1—57).—Pure bilirubin is, in time, completely converted into biliverdin by the use of a dilute solution of iodine in alcohol (N, 100). A similar oxidation occurs more rapidly by using Hübl's iodine solution of the same strength. The reaction may be denoted by the equation:



This fact may be utilised for the estimation of bilirubin titrimetrically. The requisites are (1) centinormal iodine solution in alcohol, (2) centinormal solution of sodium thiosulphate, and (3) freshly-prepared starch solution. The end reaction, namely, the characteristic colour and spectrum of biliverdin, is not seen until the bilirubin is completely changed into biliverdin. The characteristic spectrum of bilirubin is a dark band between D and E ( $\lambda$  8.8 to 9.1), and a complete absorption of light beyond  $\lambda$  4.9 and 11 in each direction. Biliverdin shows two bands, one before the D line, the other after ( $\lambda$  7.1 to 8.1, and 8.9 to 9.1), and a complete absorption of light beyond 6.4 and 14 in each direction. 1 c.c. of centinormal iodine solution = 0.00127 gram iodine = 0.00144 gram bilirubin.

The percentage of bilirubin in ox-bile varies from 0.024 to 0.027. The quantity of biliverdin is very much less, in spite of the green colour of the fresh bile. The specimens examined were found to be slightly acid. Saponifiable substances were only present in minimal quantities. Pig's bile contains from 0.051 to 0.206 per cent. of bilirubin. It is richer in urobilin and is more viscid than ox-bile. It also contains a red pigment of uncertain nature, soluble in acid amyl alcohol. It is slightly acid, rather more so than ox-bile. Saponifiable substances are absolutely small in amount, but relatively thrice as abundant as in ox-bile. Dog's bile and human bile are also slightly acid. Human bile contains 0.154 to 0.262 per cent. of bilirubin.

The acidity and amount of saponifiable substance were greater in the specimens of human bile examined than in those of the lower animals.

W. D. H.

**Glycerophosphoric acid.** By K. BÜLOW (*Pflüger's Archiv*, 57, 89—92).—The amount of glycerophosphoric acid was determined in a dog's urine by first precipitating the phosphates, then evaporating the filtrate nearly to dryness with hydrochloric acid: the phosphate so formed was then estimated. The amount averaged 0.000119 per diem. It was very slightly increased by the administration of glycerophosphates, either by the mouth or subcutaneously, and not at all increased by salol. It thus appears that the glycerophosphoric acid obtained from the lecithin of the food, or given as such, is, in great measure, destroyed in the organism; only traces pass out unchanged. The experiments with salol show that phosphoric acid does not, like sulphuric acid, form ethereal hydrogen salts with phenol-like substances.

W. D. H.

**Physiological Action of certain Derivatives of Benzaldehyde.** By K. BÜLOW (*Pflüger's Archiv*, 57, 93—96).—The four substances investigated—hydrobenzamide, benzylidenediformamide, benzylidenediacetamide, and benzylidenediureide—agree in that they are all easily broken up into their components by dilute cold mineral acids.

Hydrobenzamide led, in dogs and rabbits, to the appearance of hippuric acid in the urine. There were also symptoms of acid poisoning, which, in rabbits, proved fatal.

Benzylidenediacetamide was given to a dog. The greater part appeared as such in the urine. Hippuric acid was not present, and ethereal hydrogen sulphates were not increased.

Benzylidenediformamide is more easily decomposed than the preceding drug, both within and without the body. The decomposition that occurs within the body is not, however, very great, there only being in the urine a small amount of hippuric acid. Ethereal hydrogen sulphates were unchanged.

Benzylidenediureide was easily split in the body into urea and benzaldehyde, the latter passing out in the urine as hippuric acid.

Other benzaldehyde-derivatives (amarin, methylamarin, lophin) were investigated. The two first produced loss of appetite and sickness, and amarin produced convulsions also. Lophin had no such action. No details are given of the urine.

W. D. H.

**Physiological Action of Pyridine.** By T. L. BRUNTON and F. W. TENACLIFFE (*J. Physiol.*, 17, 272—276).—From experiments on frogs, guinea-pigs, and rabbits, the following conclusions are drawn.

1. Pyridine is not, as compared with its derivatives, an active poison; it would hardly be expected to be so, *a priori*, as it is an exceedingly stable substance.

2. Its action is almost confined to the sensory part of the nervous system. In small doses it has a stimulating, in large doses a direct paralyzing action on the cardiac muscle.

W. D. H.

**Piperazine.** By BIL-ENIHAI (*Virchow's Archiv*, 137, 51—77).—Piperazine is here extolled as a drug in gout and allied manifestations of the uric acid diathesis. It is stated to possess a powerful solvent action on uric acid deposits and calculi. W. D. H.

**Phloridzin Diabetes.** By P. A. LÉVENE (*J. Physiol.*, 17, 259—271).—Some observers think that phloridzin glycosuria is the result of a simple elimination of sugar from the organism by the kidneys; others see in it an excessive formation of glucose. The first base their view on the slight decrease of sugar in the blood after the injection of the drug, and on the fact that after the extirpation of the kidneys the quantity of sugar in the blood is somewhat increased in some cases. But no one has succeeded in establishing a fixed relation between the quantity of sugar in the blood and the sugar eliminated. In the present research on dogs, a decrease of sugar in the blood was noted in some experiments when the phloridzin was injected after ligation of the renal vessel. Cornevin (*Compt. rend.*, 116, 263) showed that phloridzin greatly increases the quantity of sugar eliminated by the milk. Consequently the poison does not affect the kidneys only. The operation of extirpation of the kidneys is not considered decisive of the question of the origin of the glycosuria.

As to the second view, that there is an increased production of sugar, and that, more especially, by the kidneys, it is found that the venous blood of the kidneys in phloridzin glycosuria contains, in some cases, more sugar than the arterial, and that the quantity of sugar in the kidney tissue itself increases after the injection of phloridzin.

Finally, the composition of the blood in phloridzin diabetes testifies to the decomposition of proteids rather than to a mere elimination of sugar. W. D. H.

## Chemistry of Vegetable Physiology and Agriculture.

**Influence of Chlorides on Nitrification.** By J. CROCHETELLI and J. DUMONT (*Compt. rend.*, 119, 93—96).—When potassium chloride is added to a soil containing calcium carbonate, the drainage water contains calcium chloride. Direct experiments show that the latter salt has a distinctly retarding influence on nitrification. If, however, the soil is washed with a small quantity of water, the retarding effect disappears, and soil which has been mixed with potassium chloride and then washed shows a marked increase in nitrification. This fact explains the different effects produced on crops by alkali chlorides in dry seasons and in rainy seasons. Large proportions of potassium chloride, however, retard nitrification under any conditions.

Sodium chloride behaves similarly, probably because in soils rich in potassium compounds it is first more or less completely converted into potassium chloride.

The efficiency of potassium chloride in promoting nitrification is

due entirely to its conversion into potassium carbonate by contact with calcium carbonate, for it produces no effect on soils that do not contain calcium carbonate.

C. H. B.

**Composition of Honey Dew, and its Influence on the Constitution of Honey.** By E. v. RÄTNER (*Z. f. a. n. Chem.*, 35, 397—405).—Honey dew is a viscid, saccharine substance found on the leaves of various plants, especially in warm, dry summers. It is partly an exudation from the leaves themselves, and is partly excreted by aphides. It is collected by bees as one of the materials for their honey. It was unusually copious in 1893, and the author collected a large specimen by rinsing the leaves of the maple with cold water. Samples of honey of the same season were also examined. The analysis of the honey dew showed much cane sugar, a little inverted sugar, and much unfermentable dextrin, together with ash and nitrogenous substances. A specimen of the dextrin was prepared from the residues of the fermentation, and found to have a specific rotatory power  $[\alpha]_D^{20} = 181.5$ , to be almost free from reducing action on Fehling's solution, and to be very slowly diffusible. In addition, there was obtained evidence of a substance, seemingly of the dextrin class, which furnished alcohol on fermentation, but was incapable of reducing copper solution. The honey samples showed abnormally large amounts of fermentable and non-fermentable, dextro-rotatory, but not copper-reducing, constituents (dextrins), the latter of which was, however, much more diffusible than that of honey dew. The author attributes the presence of these substances to contamination with honey dew, and suggests that the superior diffusibility of the dextrin in honey is due to some change which has occurred in the honey gland of the bee. On this ground, he concurs in the proposal of Haenle (this vol., ii, 164), to examine honey by dialysis, but advises that the fermented honey should be employed, since the sugars of unfermented honey dialyse out very slowly. The presence of this hitherto overlooked fermentable dextrin in genuine honey accounts for the fact that all analyses show a deficiency. The amount fermented depends, however, on the kind of yeast used.

M. J. S.

**Composition of the Seeds and Etiolated Sprouts of Hemp (*Cannabis sativa*) and Sunflower (*Helianthus annuus*).** By S. FRANKFURT (*Landw. Versuchs-Stat.*, 45, 153—154; compare this vol., ii, 113).—A further examination of hemp seeds showed that they contain, besides choline, a second base, identical with E. Jahn's trigonelline,  $C_8H_7NO_2$  (Abstr., 1886, 85, and 1886, 166), obtained from *Triyonella frumum gracum*. The author has also obtained this base from peas.

N. H. M.

**Substances occurring with the Waxy Matters of some Fruits and their Skins.** By W. SEIFERT (*Landw. Versuchs-Stat.*, 45, 29—35; compare this vol., i, 256).—The fruits examined were apples, pears, plums, bilberries, and sloes. The substances were extracted with chloroform, and the residue obtained, after distilling off the chloroform, extracted with light petroleum in a Soxhlet apparatus.

The undissolved portion was then crystallised from alcohol. The waxy matter dissolved in the light petroleum was freed from chlorophyll by extracting it with alcohol.

Apple peel yielded a quantity of waxy matter and a good deal of a substance resembling vitin in many respects. It forms a yellowish-white, amorphous powder, which when heated becomes brown and melts at  $234^{\circ}$ . It could not be crystallised from alcohol, is insoluble in water, nearly insoluble in light petroleum, but rather readily soluble in alcohol, ether, and chloroform. Its solution in strong sulphuric acid is orange-red. With acetic anhydride and a few drops of sulphuric acid, it gives a reddish-violet coloration, which becomes cherry coloured on adding more acid. The waxy substance is nearly white, melts at  $64^{\circ}$ , and when heated has an intense odour, resembling that of amyl alcohol.

Pear skin gave a wax melting at  $68^{\circ}$ , and an amorphous substance melting at  $246^{\circ}$ ; the latter resembles the compound obtained from apples in solubility, gives a brownish-yellow solution in sulphuric acid, and an intense purple coloration with acetic anhydride and sulphuric acid. The solution becomes slightly fluorescent when much acid is added.

Bilberries gave a wax melting at  $71^{\circ}$ , and a crystalline compound, probably vitin. It forms white, concentrically grouped needles with a silky lustre, melting at  $255-260^{\circ}$  after darkening. The specific rotation  $[\alpha]_D = +60.72^{\circ}$ . It resembles vitin in its behaviour towards sulphuric acid, and towards acetic anhydride and sulphuric acid. The calcium and copper salts were prepared and analysed.

Ripe plums yielded a small quantity of a substance resembling vitin, and a wax melting at  $64^{\circ}$ .

Fresh, ripe sloes yielded a wax melting at  $67.5^{\circ}$ , and an amorphous substance which melted at  $223-230^{\circ}$ , and gave similar colour reactions to the compounds already described. The alcoholic solution when treated with potash or ammonia showed an intense blue fluorescence, due to the presence of a second compound which could be dissolved out with hot water.

Tables are given showing the absorption spectra of the solutions of the compounds. N. H. M.

**Can Non-Leguminous Plants fix Free Nitrogen?** By F. NOBBE and L. HILFNER (*Landw. Versuchs-Stat.*, 45, 155-159).—After it was established that Leguminosæ, when suitably infected with nodule bacteria, have the power of assimilating free nitrogen, the authors showed that under similar conditions the same holds good with *Elaeagnus*, and with the white and black alder. *Podocarpus*, a conifer, which also has root nodules, seems likewise to have the power of fixing nitrogen. The same property has recently been frequently attributed also to non-leguminous plants, which have no root nodules, the evidence being that the final nitrogen in the plants and soil was greater than the initial nitrogen in the seeds and soil.

In the first experiments now described, mustard was grown in sand and supplied with different amounts of nitrogen. Like leguminous plants when free from nodules, the growth of mustard depended

entirely on the amount of nitrate given, and there was no assimilation of free nitrogen.

Peas, mustard, buckwheat, and oats were next grown in a mixture of sand and garden soil. The mixture was first sterilised, and then seeded with an extract of pea, mustard, buckwheat, and oat soils. Seeds were sown three times. In the case of the first crops, all the plants grew well; in the second, there was a marked falling off in the case of the non-leguminous plants, which soon showed nitrogen hunger.

The following table includes all three crops.

	Nitrogen (grams).				
	Initial.		Final.		
	In soil.	In seeds.	In soil.	In produce.	Gain.
Peas.....	3·320	0·401	3·399	0·859	0·537
Mustard.....	3·320	0·018	3·269	0·305	0·236
Buckwheat.....	3·320	0·027	3·326	0·276	0·255
Oats.....	3·320	0·048	3·618	0·487	0·737
Fallow.....	3·320	—	3·374	—	0·054

There was thus a gain in every case, even more with oats than with peas. The slight gain in the fallow plot is within the error of experiment. The following conclusions are drawn from these results.

The pea alone collects nitrogen for its own use, the three other plants, notwithstanding the increase of nitrogen in the soil, did not thrive. Peas, and doubtless all nodule bearing plants, occupy an isolated position as regards nitrogen fixation, and do not differ from other plants merely in degree. The non-leguminous plants did not themselves fix the nitrogen by which the soil was enriched; the fixation must have taken place in the soil itself, probably as the experiments of Winogradsky, Berthelot, and others indicate, by means of soil bacteria. The nitrogen so fixed does not seem to be immediately available for plants, and probably has first to be nitrified.

N. H. M.

## Analytical Chemistry.

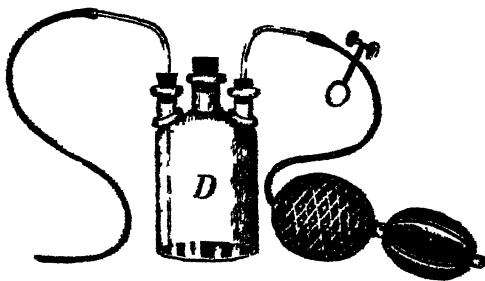
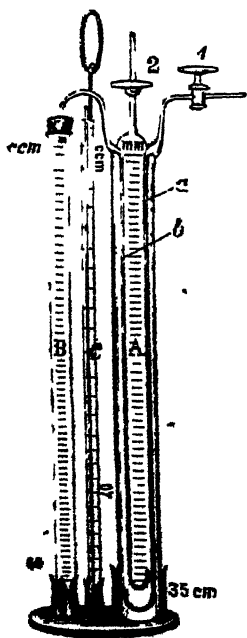
**Applications of the Gas Baroscope.** By G. BODLÄNDER (*Zeit. anorg. Chem.*, 1894, 425—431).—The author recommends the use of his gas baroscope (this vol., ii, 440) in the analysis of commercial products. Carbonates are decomposed by excess of acid; bleaching powder, pyrolusite, and potassium permanganate are decomposed by means of

hydrogen peroxide. Carbon in iron is estimated by heating the sample with sulphuric and chromic acids, without previous separation of the carbon, in an Ullgrén's apparatus, which is directly connected with the baroscope. Oxalic acid or oxalates are best treated with a mixture of dilute sulphuric acid and potassium permanganate. Manganese may be estimated in steel by first treating the sample with nitric acid and potassium chlorate, and finally treating the manganic dioxide with sulphuric acid and oxalic acid. Potassium permanganate may in turn also be checked by means of sulphuric acid and oxalic acid.

L. DE K.

**A Simple Apparatus for Measuring Gases.** By C. KIPPENBERGER (*Zeit. angew. Chem.*, 1894, 517—520).—The apparatus consists of a cylinder, A, provided with a calibrated scale divided to 0.1 cm. Inside are placed two bent tubes, *a* and *b*, which are so constructed that they both have the same capacity, and that when the apparatus is filled the meniscus of the liquid in each is in the same line with that in the stop-cock, 2. B is a cylinder calibrated to 0.1 c.c., and C a similar one, though somewhat narrower, and consequently holding less liquid, and also having an inside tube calibrated to 0.1 c.c., and closed by means of an india-rubber tube.

The apparatus is filled by connecting the tube *b* with a Woulff's bottle by means of an india-rubber tube. The Woulff's bottle is filled with any suitable liquid, which is forced out by means of the rubber force-pump.



The apparatus is intended for collecting any gas in the cylinder A. The tube *a* must be first emptied by rapidly passing through it a current of a gas soluble in the liquid. The gas to be measured is then introduced and removed from the generating flask by a further current of the soluble gas. If, for instance, hydrogen is to be estimated in presence of carbonic anhydride, the cylinder A is filled with aqueous potash, which absorbs the carbonic anhydride whilst the hydrogen is collecting on the top, displacing an equal volume of liquid which, after

being expelled through the tube *b*, is measured in B. When great accuracy is wanted, the tube C is used: as soon as the gas has been collected in the cylinder A, the tube *b* is connected with the inner tube of C, which must be completely immersed in water or any other suitable liquid. If now from any cause a contraction of the gas in A should take place, a corresponding diminution of volume of liquid in C is noticed, which must then be deducted from the measured quantity of liquid in the tube B.

By means of the centimeter scale on A, the extra pressure inside can be ascertained. The volume of gas is read off in millimeters, and this corresponds with double the height of the column of liquid, the difference being regarded as extra water pressure, which may be reduced to mercury pressure by dividing by 13.6, and must then be added to the observed barometric pressure. The volume of gas ascertained by measuring the liquid in B is then, as usual, corrected for temperature and vapour tension as well as for pressure.

L. DE K.

**Apparatus for Volumetric Analysis.** By D. SIDERSKY (*Zeit. anal. Chem.*, 35, 438—440).—The author has devised a stand, which carries two burettes and two bottles of standard solutions. The latter are Woulff's bottles with two necks, one neck carrying a tube which enters the top of the burette and terminates at the zero, the other is fitted with an elastic ball. On squeezing the ball, the pressure of the air drives the solution over into the burette, and on releasing the pressure, the excess of liquid above the zero is returned to the bottle, followed by air until the pressure is equalised.

M. J. S.

**Methods for the Estimation of Water.** By S. L. PENFIELD (*Zeit. unorg. Chem.*, 7, 22—32).—The author recommends for the estimation of water in minerals a modification of the plan employed by Brush in the analysis of *sussexite* (*Amer. J. Sci.*, 46, 240). An ordinary hard glass tube, of about 6 mm. internal diameter, and 20—25 cm. long, is closed at one end. The substance to be examined is introduced into the bottom of this, and, the tube being held horizontally, the closed end is gradually and strongly heated. The water driven off condenses in the cool part of the tube, and as the residue is often hygroscopic, the tube is best sealed just above the substance, and drawn off. The remainder is allowed to cool, cleaned outside, weighed, the condensed moisture driven off by passing a current of air through the reheated tube, and the dry tube then again weighed. The difference of the two weighings gives the weight of the water lost by the substance under examination. The form of the tube may be altered, according to circumstances, by enlarging or contracting the closed end, or introducing bulbs for the more convenient retention of the condensed water. Whilst it is being heated, it is advisable to reduce all formation of currents in the tube to a minimum by attaching to the open end of the tube, by means of a short piece of rubber tubing, a small piece of glass tube drawn out to a capillary. If the temperature required to drive off the water is too high for a Bunsen burner or blowpipe, the closed end may be introduced into a blowpipe furnace, the projecting tube being protected



from radiant heat by screens. In this case, the portion of the tube in the furnace is protected by a roll of platinum foil, and by being surrounded with charcoal. By this method water may be correctly determined in substances where carbonic anhydride or other volatile substances are also driven off by heat. Where much carbonic anhydride is evolved, a correction at the rate of 0.0096 gram of water must be added for every gram of carbonic anhydride evolved, to compensate for the saturation moisture carried away by the gas. The method also gives very trustworthy results in cases where a substance has to be added to prevent the evolution of some volatile constituent, as, for instance, lime to prevent loss of sulphuric anhydride from ferrous sulphate.

The author also finds that moisture and carbonic anhydride may often be estimated together by heating the substance in a combustion tube in a current of dry air, and absorbing the moisture and carbonic anhydride evolved.

L. T. T.

**Detection of Alkali Perchlorates in the Presence of Chlorides, Chlorates, and Nitrates.** By F. A. GOUGH and D. A. KREIDER (*Zeit. anorg. Chem.*, 7, 13—16).—If a mixture of an alkali perchlorate with zinc chloride is fused, chlorine is evolved; zinc chloride is preferable to manganous chloride, as it is not acted on by the air. The solution to be tested is evaporated to dryness in a test-tube, and then fused with anhydrous zinc chloride; if any perchlorate be present, chlorine will be evolved. Traces of chlorine are best detected by making a cap for the tube by cutting off the two bulbs of a straight drying tube, moistening the inside of the bulbs with potassium iodide solution, and resting these, the large opening downwards, on the top of the test-tube. In this way any evolved chlorine passes through the bulbs, and the least trace liberates iodine, which may be identified by means of starch solution. The author found that as little as a milligram of perchlorate could be readily detected in this way.

If chlorates or nitrates, or other substances likely to cause evolution of chlorine are present, they must, of course, be destroyed before making the test. The chlorates are easily destroyed by once evaporating with about 5 c.c. of concentrated hydrochloric acid. Nitrates are best destroyed by evaporation with 2 c.c. of a saturated solution of manganous chloride in concentrated hydrochloric acid, and subsequent re-evaporation with 1 to 2 c.c. of concentrated hydrochloric acid. The manganese must then be removed by sodium carbonate.

L. T. T.

**Volumetric Estimation of Iodine, Iodic acid, and Iodates.** By D. VITALI (*Chim. Centr.*, 1894, i, 696; from *Bull. chim. farm.*, 1894, No. 4, *Appl. Zeit.*, 9, 164).—From the equation  $\text{SO}_2 + \text{I}_2 + 2\text{H}_2\text{O} = 2\text{HI} + \text{H}_2\text{SO}_4$ , it will be seen that, when sulphurous anhydride is added to a solution of free iodine, four equivalents of acid are formed for every two atoms of iodine; hence if the resulting mixture is titrated with normal soda, 1 c.c. of the latter will correspond with  $\frac{2 \times 127}{1000 \times 4} = 0.0635$  gram of iodine originally present. In the actual

process, sulphurous acid solution is added to the iodine solution, until the colour of the latter is nearly gone; some starch solution is then added, and more sulphurous acid, until the blue colour is just discharged; the acid liquid is then titrated with normal soda solution. The original iodine solution must be neutral, and the sulphurous acid solution must contain no sulphuric acid. Free bromine and chlorine can also be estimated in this way, the sulphurous acid being added until a drop of the solution gives no colour with a solution containing starch and potassium iodide.

Iodic acid and iodates can be estimated in the same way: each molecule gives rise to the formation respectively of 7 and of 6 equivalents of acid, as is evident from the equations  $3\text{SO}_2 + \text{HIO}_3 + 3\text{H}_2\text{O} = \text{HI} + 3\text{H}_2\text{SO}_4$ ;  $3\text{SO}_2 + \text{KIO}_3 + 3\text{H}_2\text{O} = \text{KI} + 3\text{H}_2\text{SO}_4$ .

C. F. B.

**Iodometric Studies and the Constitution of Iodide of Starch.** By C. LONNES (*Zeit. anal. Chem.*, 35, 409—436).—In the presence of a metallic iodide, starch is coloured blue by a much smaller quantity of iodine than when iodides are absent. This is especially noticeable when there are alkali carbonates in the solution, and accounts for the fact that the use of normal sodium carbonate for neutralising an arsenious acid solution does not interfere with the accurate titration of the arsenic by iodine dissolved in potassium iodide. The explanation put forward by Fresenius, that the partial conversion of the normal into the hydrogen carbonate renders it incapable of hindering the formation of the blue compound, is shown to be devoid of foundation. Extreme accuracy in the titration of arsenious acid can be attained by using normal ammonium carbonate for making the solution alkaline, and adding potassium iodide with the starch paste. Using a N 1000 iodine solution a satisfactory estimation can be made with half a milligram of arsenious acid.

When iodine is added to an alkali (whether hydroxide or carbonate), its conversion into iodate and iodide is not immediately complete. A portion remains uncombined, as is evidenced by the yellow colour of the solution, and another part produces hypoiodite. The amount remaining free varies with the kind and proportion of alkali, and decreases with lapse of time. It is greatest with the hydrogen carbonates, and smallest with the hydroxides. It is much augmented by the addition of potassium iodide. The hypoiodite exhibits greater stability in presence of alkali hydroxides (potash or ammonia) than in solutions of carbonates. It is this formation of hypoiodite which falsifies titrations of iodine by thiosulphate solutions containing alkali, since hypoiodite oxidises thiosulphate to sulphate (see also *Topf, Abstr.*, 1887, 688). The addition of potassium iodide does not hinder this action. The addition of ammonium carbonate or other alkali to thiosulphate as a preservative is therefore undesirable, and all titrations of iodine by thiosulphate should take place in acid solutions.

As regards the constitution of the blue compound, it is shown that whereas the addition of mercuric chloride prevents the production of the blue colour, this is at once restored by the addition of potassium or hydrogen iodide, in quantity a little larger than suffices for

the conversion of the mercury into iodide. This indicates that the presence of a soluble iodide is necessary to the formation of the blue compound. Although the blue compound is obtained when iodine free from hydriodic acid is added to starch, its formation is not instantaneous, and part of the iodine is combined in a form in which it is not capable of oxidising thiosulphate. When the blue compound is formed in a solution containing both hydriodic acid and free iodine, 1 equivalent of the former is removed from solution with 4 equivalents of the latter. Finally, estimations of the iodine in washed blue compounds showed that one-fourth of it was present in a condition in which it was incapable of oxidising arsenious acid. Although these results are not absolutely concordant, they confirm the view of Mylius, that hydriodic acid is an essential constituent of the blue compound.

M. J. S.

**Estimation of the Sulphur in Earth-Nut Oil.** By H. KAST and F. LAGAI (*Zeit. anal. Chem.*, 35, 470: from *Dinyl. polyt. J.*, 284, 71).—0.5 to 1 gram of substance is mixed with 100 c.c. of fuming nitric acid, and 10 grams of potassium chlorate is gradually added. After 1—2 hours at the ordinary temperature, the mixture is heated carefully on the sandbath for 12—15 hours, until oily drops are no longer visible. It is then repeatedly evaporated to dryness with strong hydrochloric acid, filtered from resin, and the sulphuric acid in the filtrate estimated as usual. Carius' method gives low results.

M. J. S.

**Estimation of Total Sulphur in Urine.** By H. SCHULZ (*Pflüger's Archiv*, 57, 57—61).—The usual manner of estimating the total sulphur in urine is to evaporate to dryness, and fuse the residue with sodium carbonate and nitre. There is probably loss in this way from the passing off of sulphurous anhydride. The method here described obviates this difficulty by collecting in water all fumes during evaporation and fusing. The apparatus devised for this purpose is figured.

W. D. H.

**Estimation of Total Nitrogen in Urine by the Schneider-Seegen Method.** By F. VOIT (*Zeit. Biol.*, 31, 168—180).—The Kjeldahl method of estimating nitrogen has the disadvantage of taking a long time to perform; this is not the case with the older method of Schneider-Seegen. The latter, however, has lately fallen into discredit, and the object of the present paper is to show that it is quite as accurate as Kjeldahl's process. The method is a modification of that of Will and Varrentrapp, adapted for the examination of urine, and briefly consists in heating the urine with soda-lime, and thus obtaining all the nitrogen in the form of ammonia.

W. D. H.

**Analysis of Commercial Sodium Nitrite.** By MASSON (*J. Pharm.*, 57, 30, 41—42).—Five grams of the nitrite are dissolved in 500 c.c. of water; 50 c.c. of this solution is transferred to a flask ( $1\frac{1}{2}$  litres capacity), diluted to 1 litre, and then titrated with a standard solution of potassium permanganate (10 grams per litre) in the following manner. A few drops of a 10 per cent.

sulphuric acid is dropped into the solution, the flask is shaken, and some potassium permanganate is immediately added; this alternate addition of acid and permanganate is continued until the pink colour becomes permanent, when the flask is at once heated over a gas flame until the colour fades; potassium permanganate and acid are then immediately added, and the flask heated anew. This cycle of operations is continued as long as the permanganate is decolorised by the solution, the final temperature of which will approximate to the boiling point.

A. G. B.

**Reduction of Arsenic acid by the Action of Hydrochloric acid and Potassium Bromide.** By F. A. GOOCH and L. K. PHILLIPS (*Amer. J. Sci.*, [3], 48, 216—218).—It has been shown in a former paper (this vol., ii, 331) that arsenic acid may be readily reduced and volatilised as chloride by distilling with hydrochloric acid and potassium iodide. The authors now propose to use potassium bromide instead. The apparatus used is essentially the same as before, but when the distillate is condensed, the liberated bromine will reoxidise the arsenic. This, however, may be prevented by adding some stannous chloride, and the arsenic may then be at once precipitated with hydrogen sulphide. The large amount of free acid prevents precipitation of the tin, and also of any trace of antimony which may be present.

L. DE K.

**Decomposition of Silicates by Ferrous and Manganese Oxides.** By R. SACHSSE and A. BECKER (*Landw. Versuchs-Stat.*, 45, 147—151).—It was previously shown (*Abstr.*, 1893, ii, 243) that when silicates are ignited with ferrous oxide, a portion of the oxide acts on the silicate, and can no longer be reduced by hydrogen to metallic iron. More exact experiments were made with ferrous oxide and with manganese oxide, as it was hoped that it might be possible, owing to the different behaviour of the various silicates, to effect a separation of single soil constituents, but inasmuch as all silicates, and even quartz, are more or less attacked, no separation could be made in this manner.

The results of comparative experiments, in which kaolin, orthoclase, and quartz were ignited with ferrous and manganese oxides respectively, show that manganous oxide is a stronger reagent than ferrous oxide. This does not, however, prevent the partial reduction of ferrous oxide in presence of an excess of manganous oxide.

When iron-kaolin (prepared by precipitating ferric chloride solution with water glass) was mixed with manganese dioxide and ignited in a current of hydrogen, only a small amount of metallic iron was formed.

N. H. M.

**Volumetric Separation of Hydroxides, Carbonates, and Bicarbonates.** By C. KIPPENBERGER (*Zeit. angew. Chem.*, 1894, 495-501).—The author recommends using some new indicators, the advantage of which will be perceived by perusing the table below:—

By	Hematoxylin.	Gallein.	Alkannin	Gentiana blue.	Lyons blue.	Portier blue.
Hydroxide .....	Blue	Blue	Blue	Dark blue	Red	Red.
Alkali { carbonate .....	Red	Blue changing to red	Blue	Red	Red	Red in strong solution; blue in dilute.
Barium, Strontium, or Calcium { bicarbonate .....	Red	Red	Red	Blue	Blue	Blue.
Magnesium { carbonate .....	Blue	Blue	Blue	Blue	Blue	Blue.
{ bicarbonate .....	Red	Red	Red	Blue	{ Red Blue }	Blue.

In titrating carbonates, it must be borne in mind that during the first stage half the alkali passes into bicarbonate. This, of course, is only true when the standard acid is very dilute and is added in very small portions at a time. To better prevent loss of carbonic acid, the titration is performed in a narrow cylinder provided with a glass stopper. The reagents are generally used in alcoholic solutions.

L. DE K.

**Estimation of Sodium Hyposulphite.** By E. H. EKKER (*Rec. Trav. Chim.*, 13, 37—45).—The methods at present in use for the estimation of the amount of sodium hyposulphite in its solutions do not give very satisfactory results, and the author has therefore re-investigated the subject. He finds that potassium ferricyanide is a very suitable reagent for the purpose, as it is not affected by sodium hydrogen sulphite, but is at once converted by the hyposulphite into a ferrocyanide. The liquid to be tested is placed in a flask from which all air is driven out by hydrogen, nitrogen, or carbonic anhydride, any free acid neutralised with soda, and a small quantity of ferrous ammonium sulphate added as indicator: the standard solution of potassium ferricyanide is then added until the solution assumes a blue colour.

In order to determine the nature of the action which takes place, the author dissolved varying quantities of pure zinc in solutions of sodium hydrogen sulphite; on estimating the quantity of potassium ferricyanide required to oxidise the hyposulphite formed, he found that 1 mol. of ferricyanide was equivalent to 1 atom of zinc. According to Schützenberger, sodium hyposulphite has the formula  $\text{NaHSO}_2$ , and its formation is represented by the equation



whilst, according to Bernthsen, it has the composition  $\text{Na}_2\text{S}_2\text{O}_4$ , and is formed as follows.



In order to obtain evidence as to which of these views is correct, known quantities of sodium hydrogen sulphite solution were well shaken with zinc, in the cold, until no further action took place, and the quantity of dissolved zinc was then estimated. It was found that 1 gram of sodium hydrogen sulphite is equivalent to 0.154 gram of zinc, which agrees with the requirements of the second of the above equations, thus affording renewed confirmation of Bernthsen's formula for hyposulphurous acid.

H. G. C.

**Assay of Zinc Dust.** By F. MEYER (*Zeit. anorg. Chem.*, 1894, 435).—The author believes that his apparatus is preferable to the one proposed by Bach (this vol., ii, 332—400), and that it may also be used for other purposes, such as the estimation of carbonic anhydride in carbonates. In this case, the dilute sulphuric or hydrochloric acid should be first saturated with carbonic anhydride, best by introducing a small quantity of sodium hydrogen carbonate. The apparatus without the generating flask may also be used for collecting and measuring any gas under atmospheric pressure, provided its volume is between 260 and 400 c.c.

L. DE K.

**Employment of Mercuric Oxide in Analysis.** By E. F. SMITH and P. HEYL (*Zeit. anorg. Chem.*, 7, 82—90).—The use of mercuric oxide has been recommended by Berzelius and by Volhard (a) for precipitating some of the metals from their solutions, and (b) for converting chlorides, sulphides, &c., into oxides for weighing. The

authors have investigated this subject, to determine in which cases this reagent can be advantageously used.

For preparing oxides for weighing, the precipitate (sulphide, &c.) is dissolved in a little hydrochloric acid, evaporated to a small bulk, and introduced into a crucible; excess of mercuric oxide is then added, and some strewn over the moist inner sides of the crucible, the whole is slowly dried on a hot plate, and finally heated strongly, to drive off all mercuric chloride and oxide. In this way, zinc sulphide may be readily and quickly converted into oxide for weighing. Cadmium gives good results if care is taken to well powder the sides of the crucible, and not to allow the crucible to become red-hot until the fumes of mercuric oxide have entirely disappeared; otherwise, some of the cadmium chloride may be volatilised before its conversion into oxide. Manganese and nickel sulphides, and bismuth oxychloride give good results. Cobalt does not give a sufficiently definite oxide to be satisfactory, the final product varying in composition between  $\text{Co}_2\text{O}_3$  and  $\text{Co}_3\text{O}_4$ , according to the temperature, &c.

For separating metals by precipitation, mercuric oxide may safely be used to separate iron from manganese in cold solutions, although the first precipitate should be redissolved and reprecipitated to ensure freedom from traces of manganese. It may be used as a quick, approximate method of separating iron from nickel or cobalt, if absolute accuracy is not required. Chromium is also precipitated from its cold solutions. Zinc, nickel, cobalt, uranium, beryllium, cerium, and lanthanum are only partially precipitated in the cold.

L. T. T.

**Reaction of Copper Salts.** By H. THOMAS (*Zeit. anal. Chem.*, 35, 464; from *Pharm. Centr.*, 31, 31).—If to a solution of cupric sulphate in 200,000 parts of water, which is too dilute to give a visible coloration with potassium ferrocyanide, potassium iodide is added, a yellow coloration is produced, becoming violet with starch paste. The latter coloration is visible even with 500,000 parts of water. M. J. S.

**Quantitative Analysis by Electrolysis.** By A. CLASSEN (*Ber.*, 27, 2060—2061).—A description is given, accompanied by plans and a sketch, of the manner in which the private laboratory, and a bench in the inorganic laboratory, are fitted up for electrolysis at Aix-la-Chapelle. At the bench, 24 electrolyses can be simultaneously carried out, and the current in each electrolytic cell can be measured by means of an ampère-meter common to the set. The usual method of measuring the current with a gas voltameter before the electrolysis is commenced is very faulty. The author uses an ampère-meter, which can be thrown into circuit during electrolysis by adjusting a copper bridging-wire between two mercury cups. When the measurement is made, the bridge is removed and connection made, so as to cut off the ampère-meter, but this time by means of a bridge having a resistance just equal to that of the meter; the current in the circuit thus remains equal to that at the time of measurement. The current is not quoted, but the "current-density," or the number of ampères per 100 sq. cm. of surface of the electrode. The solutions used were commonly made by adding ammonium, or occasionally potassium

oxalate to a solution of the salt of the metal, some free oxalic acid being also usually added. In the case of antimony, however, sodium sulphide was added, and, in the case of silver, potassium cyanide. The deposits were dense and metallic. With lead, the electrolysis was carried out in the presence of nitric acid only, and the deposit of peroxide weighed as such. With manganese, it was done in the presence of acetic acid only, and the precipitate of peroxide was ignited and weighed as  $MnO_2$ . In the case of mercury, tin, antimony, lead, and manganese, it was found expedient to use, not a polished platinum dish, but one the surface of which had been made matt by means of a sand blast; the deposit often adhered to this, when it would not adhere to a smooth surface. Below are given details of current-density in amperes, difference of potential of the electrodes in volts, temperature, and duration of the electrolysis as employed in depositing various metals.

	Current-density, amperes.	Diff of potential, volts.	Temp.	Time, hours.
Copper .....	1.0—0.35	3.2—2.5	19—60°	2—2½
Cadmium .....	1.0—0.5	3.5—2.75	64—76	3—3½
Zinc .....	1.0—0.5	4.8—3.5	55—60	2
Iron .....	1.5	3—4	20—15	½—1
Nickel .....	1.0	3.0—3.5	60—70	2½—2½
Cobalt .....	1.0	3.0—3.5	60—70	2½—2½
Mercury .....	1.0—0.2	4.7—2.6	23—37	1½—5½
Silver .....	0.5—0.2	4.4—3.3	20—30	1½—5
Tin .....	0.3—1.0	3.2—4.2	25—30	5½—6½
Antimony .....	1.5—0.3	1.5—0.85	25—60	2—17½
Lead .....	1.65—1.45	2.5—2.4	60—67	1—1½
Manganese .....	0.3	4.9—4.3	50—65	3

Similar details are also given for the separation of lead and copper, copper and iron, antimony from arsenic and from tin, copper from nickel and from cobalt, iron from aluminium and from chromium, and for the simultaneous deposition of iron and cobalt and of iron and nickel. The methods used are already well known. C. F. B.

**Colorimetric Estimation of Minute Quantities of Lead, Copper, Tin, and Iron.** By E. R. BUDEN and H. HARRY (*Analyst*, 19, 160—175).—The authors having tried the various processes in use for the colorimetric estimation of traces of these metals in mineral waters, lemonades, &c., came to the following conclusions.

That in determining traces of metals by the hydrogen sulphide process (compare *Abstr.*, 1883, ii, 242, 599), it is, above all, necessary to follow strictly the same order in the addition of the reagents, and, as closely as possible, to use always the same quantity of the reagent, both in the actual experiment and in the preparation of the solution used for the comparative determination. That all the conditions of experiment should be similar; for instance, in testing a lemonade, the liquid for comparison should contain the same amount of sugar, acid,



&c. Even the amount of carbonic anhydride in effervescing beverages exercises a slight influence on the reaction. The authors promise further experiments and invite co-operation. L. DE K.

**Estimation of Manganese, Magnesium, Zinc, Cobalt, and Nickel by Classen's Oxalate Process.** By G. NASS (*Zeit. angr. Chem.*, 1894, 501—508).—Classen recommends adding a solution of potassium oxalate in excess and then precipitating the metallic oxalate by boiling with excess of acetic acid. The precipitate is then washed with a mixture of alcohol and acetic acid and at once ignited. The author, having tried the process with both potassium and ammonium oxalate, finds that it is perfectly useless for manganese, cobalt, and nickel, but that good results are obtained with magnesium and zinc. L. DE K.

**Estimation of Ferrous Iron in Silicates.** By J. H. PRATT (*Amer. J. Sci.*, [3], 48, 149—151).—The author dissolves the mineral in a boiling mixture of hydrofluoric and dilute sulphuric acids. To prevent oxidation, the solution is effected in a current of carbonic anhydride. The apparatus used consists of a Rose's ignition crucible, which must, however, be entirely made of platinum. After cooling, the liquid is transferred to a beaker or dish, and titrated with permanganate. The test analyses are very satisfactory. L. DE K.

**Separation of Bismuth, Zinc, and Nickel by Hydrogen Peroxide.** By P. JANNASCH and E. ROSE (*Ber.*, 27, 2227—2231; compare *Abstr.*, 1892, 537; 1893, ii, 492; this vol., ii, 32, 71).—Bismuth may be separated from zinc or nickel by pouring a solution of the nitrates of the metals in 5 c.c. of nitric acid and 50 c.c. of water into a mixture of 25 c.c. of 3—4 per cent. hydrogen peroxide and 15 c.c. of concentrated ammonia. Under these circumstances, the bismuth is completely precipitated as the hydrated peroxide, which is then collected and washed, first with dilute ammonia, finally with cold water. Only traces of zinc or nickel are precipitated along with the bismuth, so that, unless exceptional accuracy is required, it is not necessary to redissolve the precipitate and repeat the separation. The dried precipitate is removed from the filter paper, the latter carefully incinerated, and the ash treated with nitric acid; the precipitate is then added to the ash, and the whole carefully heated, a platinum crucible being used. The silica, which is usually present in hydrogen peroxide to the extent of about 0.006 gram per 50 c.c., is precipitated along with the bismuth, and must be allowed for.

The zinc or nickel is determined in the residue obtained by evaporating the filtrate after it has been carefully ignited to remove ammonium salts.

The authors have found that ammonium persulphate may often be employed as a reagent instead of hydrogen peroxide, but that it is not so convenient. A. H.

**Rapid Detection of Tin.** By G. DENIGÈS (*J. Pharm.*, [5], 30, 207—212).—Various organic compounds are capable of immediately producing a blue coloration in a solution of sulphomolybdic acid

(ammonium molybdate, 10 grams; water, 100 c.c.; pure sulphuric acid, 100 c.c.). Among inorganic compounds, hypophosphites in hot solution, and hyposulphites, ferrous salts, cuprous salts, and stannous salts, at the ordinary temperature, produce the blue colour immediately.

Notwithstanding the presence of these other reducing agents in a solution, tin may be rapidly detected by the following method. Several drops of the suspected solution is placed on a piece of platinum with a drop of sulphuric acid, and a piece of zinc is brought in contact with the platinum underneath the surface of the liquid. After a minute or two, the platinum is washed with water, 4 or 5 drops of hydrochloric acid are dropped upon the spot, and the liquid evaporated to dryness at a gentle heat. 3 or 4 drops of water are then added to the residue, left there for some seconds, and 1 or 2 drops of the solution thus formed is poured into 2 or 3 drops of the sulphomolybdic acid; an instantaneous blue coloration indicates that tin must have been on the platinum, for, owing to the insolubility of cuprous chloride, this will not be dissolved by the water.

In alloys, tin may be rapidly detected as follows. Some particles of the alloy are placed in a capsule with a dozen drops of hydrochloric acid, which is then evaporated to dryness at a gentle heat. A few drops of water is now placed on the residue, and 1 c.c. of a nearly boiling solution of cacotheline is added. If tin be present, an amethyst colour is produced, which becomes blue with alkali in the absence of air, and green in the presence of air. The cacotheline solution is prepared by dissolving 0.5 gram of brucine in 5 c.c. of cold nitric acid in a flask, adding 250 c.c. of water, boiling for 10 to 15 minutes, and making up the volume of the cooled liquid to 250 c.c. If the tin is present in very small quantity, the amount of this reagent added should be limited to 4 or 5 drops; ferrous and cuprous salts do not yield the reaction. One-twentieth of a milligram of tin can be detected in a drop of liquid by this test.

Since metastannic acid is readily reduced to tin in the presence of zinc and hydrochloric acid, it can be readily identified by placing it on a sheet of zinc and moistening it with hydrochloric acid; the spot of zinc, on which the tin has been thus deposited, may be dissolved in acid and the tin detected by the tests described above.

A. G. U.

**Separation of Tin from Antimony.** By MENGIN (*Compt. rend.*, 119, 224—226).—The alloy containing tin and antimony is treated with nitric acid, which dissolves the other metals and converts the tin and antimony into insoluble oxides, which are washed, heated, and weighed together. The oxides are then mixed with a plate or ball of tin and dilute hydrochloric acid, the liquid being gently heated for a few hours with occasional agitation. When all trace of the oxides has disappeared, the reduced antimony is collected on a weighed filter, washed with water and alcohol, dried, and weighed. The tin oxide has been converted into soluble chloride.

C. H. B.

**Reduction of Vanadic acid by Tartaric acid and its Titration in Alkaline Solution with Iodine.** By P. E. BROWNING (*Zeit.*

*anorg. Chem.*, 7, 158—160).—The solution of vanadic acid is boiled with an excess of tartaric acid until it acquires a beautiful blue colour; it is then mixed with excess of potassium hydrogen carbonate, cooled, and treated with excess of standard iodine solution. When the blue coloration of vanadium tetroxide has disappeared, the excess of iodine is titrated with a solution of arsenious acid until the colour of the iodine is just discharged, finally the blue coloration should be obtained when a few drops of iodine solution and starch are added.

The results agree very well with those obtained by reduction with sulphurous acid and titration with permanganate. E. C. R.

**Analysis of Gold Ores.** By S. COTTON (*J. Pharm.*, [5], 30, 85—87).—1 kilo., or more, of the ore is finely powdered, roasted at a dull red heat to expel sulphur and arsenic, and made into a cream with water; 100 grams of mercury is added and the whole is shaken from time to time. After two days, 100 grams of potassium cyanide is added, and the intermittent shaking is continued for another two days. The mixture is dried, and the mercury, which now contains all the gold, is separated, partly directly and partly by washing, and the greater portion of the metal dissolved by nitric acid; the remainder is expelled by heat in an open crucible. The gold is thus left ready to be weighed. The process is capable of estimating quantities of gold, which cannot be determined by the usual lead assay.

A. G. B.

**Modifications of Romijn's Apparatus for the Estimation of Dissolved Oxygen in Water.** By J. C. BOUW (*Rec. Trav. Chim.*, 13, 88—92; compare Romijn, this vol., ii, 28).—The apparatus is shown in Fig. 1. The flask A has a capacity of about 4 litres, and is fastened by bands of copper (C) to the leaden sinker B, which is mounted on a wooden plate V. The pipette H is attached to A by the copper frame KL, has a three-way cock at F, and is connected by rubber tubing to D, which is closed with a stopper attached to a string. The apparatus is lowered to the required depth, and the stopper removed from D, the flask and pipette quickly fill with water, the air escaping by the tube T. The water in the pipette is used to estimate the oxygen, that in the flask for the determination of the ammonia, &c. Fig. 2 represents an improved form of pipette (H in Fig. 1). A and B are two three-way taps, the bulb C contains about 10 c.c., its capacity between the fiducial marks M and N being accurately determined, the tube R communicates at S with the sodium hyposulphite solution, the other tube is connected with a supply of hydrogen. The sodium hyposulphite solution is introduced by turning the taps into the position shown in the figure. When the solution reaches the mark M, B is closed, and A is turned so that the bulb communicates with the source of hydrogen, the pipette is then attached to R and the solution allowed to flow through P, the liquid being afterwards drawn back to the mark N. The iodine solution is introduced in a similar manner.

This apparatus allows water to be obtained from any depth, in

FIG. 1.

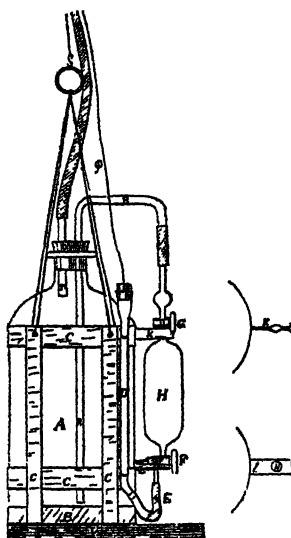
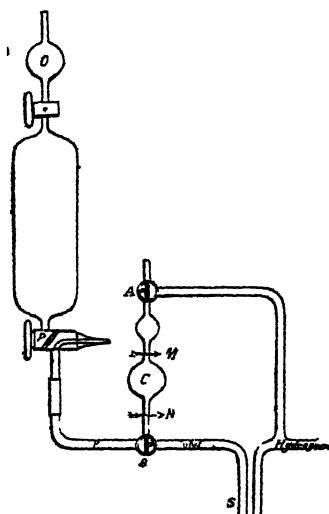


FIG. 2.



quantity sufficient to admit of the estimation of all the constituents; it is much easier to manipulate than Romijn's, and the pipette, being free from adhering water and dirt, ensures greater accuracy.

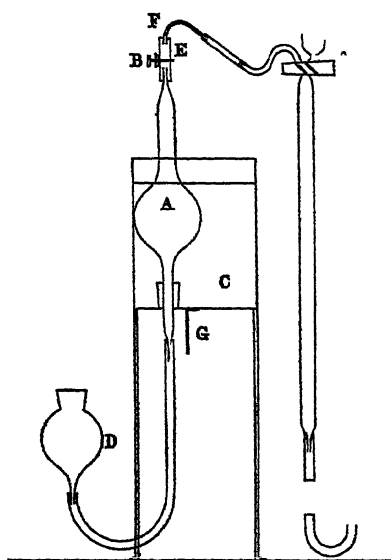
J. B. T.

**Apparatus for Collecting Samples of Water some Distance beneath the Surface.** By W. T. BURGESS (*Chem. News*, 70, 54).—This apparatus is for obtaining samples for bacteriological examinations. A partially exhausted glass tube, of 6 c.c. capacity, drawn out at the top to a narrow tube and at one point to a very fine capillary, is supported in a weighted wire holder and lowered into the water; at any desired depth, a jerk of the wire by which the tube is lowered releases a spring attached to the holder, which, flying round, breaks off the tube at the capillary. The tube fills in a few seconds, and is then drawn up and sealed.

D. A. L.

**Apparatus for the Extraction of Gases Dissolved in Water.** By S. HARVEY (*Analyst*, 19, 121—123).—The apparatus consists of a globular, spindle-shaped glass vessel A, having two opposite tapering necks, 13—14 in. long between the two extremities, the globular part being  $3\frac{1}{2}$  or  $3\frac{3}{4}$  in. in diameter. The upper neck is somewhat enlarged, tapering gradually, the lower is narrow and cylindrical; both end in a capillary bore bulbous at the end, to enable the rubber tubing to be securely affixed. The upper one has a short length of small-bore pressure tubing, securely tied and furnished with a screw clamp B. The apparatus is used as follows:—In the first place, the exact

capacity from end to end is ascertained. It is then filled with sample of water, the clamp B is closed, and the vessel carefu



fixed upright in a tin wat  
bath C, 6 in. in diameter  
7 in. high, standing on leg  
12 in. high, and having an open  
ing in the bottom closed by a  
perforated cork; the latter is s  
arranged that whilst the lower  
stem of the spindle projects 2 in  
below the bottom, the globular  
part is immersed in the bath  
The clamp is now opened  
and about one-third of the  
water allowed to run into :  
measured vessel. This amoun  
deducted from the total give  
the amount experimented on  
The lower end of the spindle  
has now one end of a 2 ft  
piece of small-bore pressur  
tubing slipped over it and se  
cured. This tubing has a mer  
cury reservoir D at the othe  
end, and the latter is firmly  
supported.

Mercury is now poured into the reservoir, the clamp B is again opened, and the air, together with any bubbles, driven out, the water being allowed to follow to the upper end of the rubber tube E. After closing the clamp, a nitrometer having a bent capillary tube, F, affixed to the beak, is filled with mercury, and this is forced to the end of the capillary tube, which is now thrust into the top of the rubber tubing and secured. The reservoir is lowered and the clamp cautiously opened in order to run a little mercury over sufficiently far to reach the lower end of the capillary tube. The clamp is now closed, the bath filled with cold water, and heat applied. To prevent the latter injuring the lower end of the spindle, a metal screen G is riveted on to the bottom of the bath so as to screen the glass from the flame, and for the same reason the hole in the bath is at one side to allow sufficient space for heating.

Under the diminished pressure, the water in the globe soon boils vigorously and without bumping, and the expelled gases collect in the upper stem. After two hours, the reservoir may be raised, the clamp B opened, and the gases passed into the nitrometer, taking care not to admit any water. The clamp is again closed, the reservoir lowered, and the operation continued to collect any further traces of gas. By raising the reservoir, any residual gas may be driven completely into the nitrometer, where it is subjected to measurement and absorption.

L. DE K.

**The Relation of Saccharimeter Degrees to Angular Degrees.**  
By E. RIMBACH (*Ber.*, 27, 2282—2285).—One scale division on the

Ventzke quartz wedge saccharimeter is usually taken as equal to  $0.3455^\circ$  or  $0.3465^\circ$  of rotation for sodium light. The author has re-determined this ratio, and finds that it increases slightly as the concentration of the sugar solution increases; he uses, as the source of light, either an ordinary gaslight or an Auer lamp with a dichromate screen. For cane sugar and glucose the mean value of the ratio is  $0.344$ ; the ratio is practically the same for solutions of santonin in chloroform and of camphor in alcohol. W. J. P.

**Gravimetric Estimation of Sugar by Fehling's Solution.** By C. KILLING (*Zeit. angew. Chem.*, 1894, 431—433).—The author states that in the otherwise excellent process of Märcker and Allihn, everything depends on the quality of the asbestos used. As the peculiar kind recommended bids fair to become very scarce, or perhaps to altogether disappear from the market, the author has again taken to the old plan of collecting the cuprous oxide on a filter. The *modus operandi* is as follows.

The filter containing the cuprous oxide is dried at  $100^\circ$ , the contents then transferred to a weighed dish, cooled in a desiccator, and weighed. The filter is now burned in a weighed porcelain crucible, ignited over the blow-pipe, and the cupric oxide finally weighed. The result will be, however, somewhat too high, as the filter paper always absorbs some copper from the Fehling's solution which washing fails to remove. This quantity is, however, fairly constant, and may be once for all determined by a blank experiment.

L. DE K.

**Estimation of Sugar by Fehling's Solution.** By A. PRAGER (*Zeit. angew. Chem.*, 1894, 520—521).—The author (see preceding abstract) prefers to operate as follows:—The cuprous oxide is collected on a double filter, washed and dried. The precipitate is now as much as possible detached from the filter, and transferred to a piece of glazed paper. The filter is incinerated in a platinum crucible, and the ash well pressed with a platinum wire. The cuprous oxide is transferred to the crucible and the ignition continued over a small flame at first, actively stirring all the while. After heating the covered crucible with the full flame for a few minutes, it is cooled and weighed. The outer filter is ignited so as to estimate the amount of copper absorbed by the paper. L. DE K.

**Estimation of Sugars by Fermentation.** By LASCHÉ (*Bied. Centr.*, 23, 551—552; from *D. Bierbrauer*, 21, 1210—1213).—In the estimation of sugar with Fehling's solution, high results may be obtained, owing to the action of the Fehling's solution on substances which are not sugars. It is, moreover, sometimes desirable to estimate single sugars. It is therefore proposed to employ certain forms of yeast which ferment one or more sugars. By fermenting, for instance, wort (500 c.c.) with Saaz yeast (2.5 grams), the amount of maltose, dextrose, and saccharose can be determined, Saaz yeast being unable to ferment the substances known as maltodextrin, or isomaltose. If instead of Saaz yeast, *Saccharomyces apiculatus* is employed, the amount of dextrose alone is obtained.

In carrying out investigations of this kind, it is necessary to know the properties of the various yeasts: that *Saccharomyces apiculatus* will only ferment sugars like dextrose; *Saccharomyces Joergensenii*, dextrose and saccharose; Saaz yeast, dextrose, saccharose, and maltose; and that Frohnberg yeast decomposes all those sugars and isomaltose as well. *Saccharomyces Kephir* may be employed for the estimation of lactose.

N. H. M.

**Examination of Urine for Small Quantities of Sugar.** By A. H. ALLEN (*Analyst*, 19, 178—184).—To detect small quantities of sugar in urine, the author operates as follows:—7 to 8 c.c. of the sample is heated to boiling in a test-tube, and 5 c.c. of solution of copper sulphate—as used to make Fehling's solution—is added. This precipitates nearly all the uric acid, xanthine, hypoxanthine, phosphates, &c. When nearly cold, 1 to 2 c.c. of a saturated solution of sodium acetate is added, which will render the precipitation complete. After filtering, 5 c.c. of the usual alkaline tartrate mixture is next added, and the mixture boiled for 15 to 20 secs. In the presence of more than 0.25 per cent. of sugar, separation of cuprous oxide occurs before the boiling point is reached, but with smaller proportions precipitation takes place during the cooling of the solution, which becomes greenish, opaque, and suddenly deposits cuprous oxide as a fine orange-yellow precipitate. The best qualitative test for traces of sugar is, however, the well-known reaction with phenylhydrazine.

L. DE K.

**Reactions of Normal and Basic Lead Acetates with Sodium Carbonate, Sulphate, and Phosphate.** By A. BORNTAEGER (*Zeit. angew. Chem.*, 1894, 454—460).—If normal lead acetate is cautiously precipitated with sodium carbonate, the filtrate is distinctly acid to delicate litmus paper; but the author finds this to be due to carbonic and not to acetic acid. The filtrate also contains a little lead, which will, however, not be the case if the acetate has been precipitated with an excess of sodium carbonate.

If normal lead acetate, which always has a slightly acid reaction, is mixed with sodium sulphate, a neutral filtrate is obtained. The end of the reaction is not so marked as with sodium carbonate, and it is therefore difficult to avoid excess of the reagent. A large excess of the latter seems necessary for the complete precipitation of the lead.

Although lead acetate has but a feebly acid reaction, and sodium dihydrogen phosphate a decidedly alkaline one, the two salts when mixed in equivalent proportions give a strongly acid filtrate which contains only traces of lead and phosphoric acid. If a slight excess of sodium phosphate is used, a filtrate free from lead is obtained.

When basic lead acetate and sodium carbonate are mixed, a neutral filtrate is obtained which contains traces of lead if no excess of the reagent has been added; traces of lead will, however, reappear on adding a large excess of the same.

From basic lead acetate and sodium sulphate, a neutral filtrate is obtained containing a small quantity of lead; this may, however,

be reduced to a mere trace by using a fairly large excess of the reagent, and allowing this to act for 24 hours.

From basic lead acetate and disodium hydrogen phosphate, an acid filtrate is obtained, which will be free from lead if the phosphate be added in large excess and allowed to act for some 24 hours.

L. DE K.

**Reactions of Normal and Basic Lead Acetates with Sodium Carbonate, Sulphate, or Phosphate in the presence of Invert Sugar.** By A. BORNTAEGER (*Zeit. angew. Chem.*, 1894, 521—528).—The author (see preceding abstract) has tried the reaction of normal and basic lead acetates with sodium carbonate, sulphate, and phosphate in the presence of invert sugar.

Sodium carbonate added in equivalent proportion does not completely precipitate the lead acetate. On adding an excess, part of the precipitate redissolves, but it gradually reprecipitates to a certain extent. The solubility is, however, not due to the invert sugar as such, but only to the levulose it contains, as dextrose has no solvent action.

Sodium sulphate, added in moderate excess only, leaves a trace of lead in solution, but a larger quantity precipitates the lead as completely as in the absence of invert sugar.

Disodium hydrogen phosphate also precipitates the lead completely.

Sodium carbonate added to a solution of basic lead acetate does not completely precipitate the lead, whilst an excess actually redissolves some of the precipitate; this, however, is reprecipitated to a certain extent after some time.

Sodium sulphate when added either in great or small excess does not completely precipitate the lead even on long standing.

Disodium hydrogen phosphate completely removes the lead from the sugar solution.

L. DE K.

**Reaction for Aldehydes: Differentiation of Aldoses and Ketoses.** By A. VILLIERS and M. FAYOLLE (*Compt. rend.*, 119, 75—77).—Carefully purified acetone has no action on a solution of magenta decolorised by sulphurous acid, but the removal of the last traces of aldehyde is extremely difficult. It follows that this reagent can be used for the detection of aldehydes in acetone; it should be prepared without excess of sulphurous acid, and the experiments should be made in closed tubes. Methyl ethyl ketone gives no coloration with the reagent, but it is desirable that a large number of other carefully purified ketones should be examined.

The reagent can also be employed to distinguish between aldoses and ketoses. Glucose, invert sugar, and galactose produce a coloration as intense as with ordinary aldehyde, but levulose and sorbitol give no reaction. About 1 gram of sugar should be added to 10 or 12 c.c. of the reagent, which should be free from acid, since the latter interferes with the reaction.

Saccharose, maltose, and lactose give no coloration, but after several days, a coloration appears, probably in consequence of a



d-composition in presence of water with formation of aldehydic glucoses.  
C. H. B.

**Valenta's Acetic acid Test.** By W. CHATTAWAY, T. H. PEARMAIN, and C. G. MOOR (*Analyst*, 19, 147—150).—The authors have adopted the following method:—A short and somewhat thick test tube of about 4 in.  $\times$   $\frac{1}{2}$  in., into which a well-fitting stopper has been ground, is chosen; 2.75 grams of the fat is then weighed into the tube, and 3 c.c. of acetic acid of exactly 99.5 per cent. strength is measured from a burette, and added to the fat. The tube is then stoppered and placed in a beaker of warm water, increasing the heat until, after shaking, the contents become quite clear. The source of heat is then removed, and the tube is so placed that it is in the centre of the beaker; the whole is then allowed to rest until the change from transparency to turbidity occurs, when the temperature is observed by means of a thermometer which has been previously attached to the test tube by a rubber band. The change is very well marked. It is of the utmost importance that the fat or oil—olive oil, for instance—should be entirely free from water. The fat should also not have been subjected to any over-heating.

The authors have tabulated the results of their experiments with a large number of oils and fats. As regards butter, figures varying from 39—29° were obtained, whilst "margarine" gave 97—94°. The test seems most useful when applied to butters, margarines, or mixtures of the two.  
L. DE K.

**Turbidity Temperature of Oils and Fats with Glacial Acetic acid.** By E. W. T. JONES (*Analyst*, 19, 151—155).—The author (see preceding abstract) having noticed that even the presence of 0.2 per cent. of water in the acetic acid makes a serious difference in the turbidity temperature, proposes to check the acid with normal butter fat. To the best glacial acetic acid, water is carefully added until the turbidity temperature with the normal butter fat comes exactly at 60°; the acid is then reserved for the testing.

It is also most important that the relative proportions of acid and fat should be strictly adhered to. The author uses special pipettes, a narrow one holding 3 grams of water at 15.5° for the acid, and wider ones, with wider orifices, delivering 3 grams of water for the fat. All oils or fats are measured at 50°.  
L. DE K.

**Stable Form of Hübl's Iodine Solution.** By P. WELMANS (*Zeit. anal. Chem.*, 35, 457; from *Pharm. Zeit.*, 38, 220).—For preparing the solution of iodine with mercuric chloride, a mixture of acetic acid with an equal volume of ethylic ether or ethylic acetate is used. The solution is fit for use immediately, and retains its strength for a long time.  
M. J. S.

**Analytical Constants of Seal Oil.** By A. C. CHAPMAN and J. F. ROLFE (*Chem. News*, 70, 1—2).—The authors have tabulated some analytical data for seal oil. Six samples (also a sample of blown oil) which were undoubtedly genuine were tested for specific

gravity, insoluble fatty acids, melting points of the same, iodine and bromine absorptions, total acidity number, saponification equivalent, free (oleic) acid, and the "Reichert" figure. The processes are fully described, but present no novel features. The lighter coloured specimens were fairly constant as regards specific gravity (0.925—0.926) and the melting point (22—23°) of their insoluble acids. The other figures show great variation.

L. DE K.

**Microchemical Examination of Quinine.** By H. BEHRFNS (*Rec. Trav. Chim.*, 13, 1—12).—In this paper, the author describes the microchemical reactions of the cinchona alkaloids, quinine, cinchonine, quinidine, and cinchonidine, and describes a method by which small quantities of the last three may be readily detected in commercial samples of quinine. The paper does not admit of being shortly abstracted, and, for the details, reference must, therefore, be made to the original.

H. G. C.

**Estimation of the Alkaloids in Strychnos Seeds.** By C. C. KELLER (*Zeit. anal. Chem.*, 35, 491—493; from *Apoth. Zeit.*, 8, 542).—Fifteen grams of the powdered substance is freed from fat by washing with ether in a tube plugged with cotton wool. The ethereal extract, amounting to 100 c.c., contains some alkaloid, which must be recovered by shaking it with 15 c.c. of N/30 hydrochloric acid and washing out the acid with 10 c.c. of water. The exhausted residue is transferred to a vessel of 250 c.c.; ether is added until the whole amount present is 100 grams, 50 grams of chloroform, and 10 grams of 10 per cent. ammonia solution are added, and the whole is shaken for half an hour. The acid solution is then added and again well shaken. When separation is complete, the ether chloroform solution is filtered, and 100 grams of it is evaporated in a tared conical flask. The residue is freed from chloroform, which it obstinately retains, by repeated evaporation with absolute alcohol, then dried at 95—100° and weighed. The purity of the alkaloid may be verified by titration with iodoquin as indicator. The proportion of chloroform to ether must be accurately observed.

M. J. S.

**Assay of "Cortex Granati."** By W. STOEDER (*Chem. Centr.*, 1894, i, 606; from *Ned. Tydschr. Pharm.*, 6, 39—44).—Gehe has stated that *cortex granati* only contains about 0.3 per cent. of alkaloids. The author, however, has generally found 1 per cent., but in the root bark only, the other varieties yielding much less. Gehe's process of extracting the bark with a mixture of ether, chloroform, and ammonia, dissolving the crude alkaloids in excess of standard sulphuric acid, and titrating back with an alkali is, however, quite trustworthy.

L. DE K.

**Analysis of Malt.** By T. CROSSMAN (*J. Amer. Chem. Soc.*, 16, [8], 559—565).—The author takes exception to some statements made by Miller on the analysis of malt (this vol., ii, 371). According to this chemist, the most important points from a brewer's view,

are: moisture, extract, diastatic power, and acidity. The author observes that these factors do not tell brewers of English beers much, although they may be useful to those who brew German beer; but when taken in conjunction with ready-formed sugars soluble in water, the uncoagulable proteids, free maltose, maltodextrin, or dextrin and unmodified starch, the results give information of the greatest possible value. The moisture should be about 1 per cent., 3 per cent. being regarded with suspicion. The extract is usually determined in England by Heron's method (*J. Soc. Chem. Ind.*, 7, 259—276), and this has always given the author the greatest satisfaction. The diastatic capacity is best determined by Lintner's process, but is not of much use unless the condition of the starch is known. The amount of ready-formed sugars should not exceed 17 per cent, calculated on the malt; it bears a relation to the proportion of soluble uncoagulable proteids, which, according to Moritz, is represented by the factor 63.

After calling attention to the great importance of the estimation of free maltose and maltodextrin, the author gives his own process for the estimation of the unmodified starch ("steeliness"). Fifty grams of malt is mashed as usual, then boiled vigorously for one hour, and then cooled to 150° F.; 50 c.c. of a cold-water extract (prepared by soaking 50 grams of ground malt for four hours in 500 c.c. of water) is now added, and the mash kept at 150° F. for one hour longer. It is then cooled down and made up to 515 c.c. The gravity is taken, allowance being made for the gravity caused by the cold-water extract. The difference in solid matter between boiled mash and mash gives the amount of unmodified starch, which should not exceed 7 per cent.

L. DE K.

**Estimation of Bilirubin in Bile.** By A. JOLLES (*Pflüger's Archiv*, 57, 1—57).—See this vol., ii, 466.

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# ERRATA.

VOL. LXIV (ABSTR., 1893).

## PART I.

Page	Line	
411	2*	for "G. MAZZARA" read "G. MAZZARON."
15	6	„ "J. A. JESURIN" read "J. A. JESURUN."

## PART II.

601	20*	„ "not fermented" read "fermented," and for "suffers fermentation" read "not."
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VOL. LXVI (ABSTR., 1894).

## PART I.

73	14*	} „ "S. K. DZIERZGOWSKY" read "S. K. DZIERZGOWSKY."
234	23*	
136	13*	} „ "nitrobenzal-β-dinaphtholmethane" read "nitrophenyl-β-dinaphtholmethane."
	5*	
187	3	
	7	„ "metanitrobenzal-α-dinaphthylamine" read "metanitrophenyl α-dinaphthylamine."
184	1	} „ "acetonecarboxylic acid" read "acetonedicarboxylic acid."
	7	
264	16*	} „ "ammonia" read "ammonium chloride."
	15*	
	14*	
411	13	„ "NlPh·CS·NPh·N·CHMe <sub>2</sub> " read "NHPh·CS·NPh·N·OMe <sub>2</sub> ."
429	18	„ "n-Phenylpyrazolene" „ "n-Phenylpyrazolone,"
451	26	„ "C. ABERHART" read "C. EBERHARDT."

## PART II.

6	10*	In the original paper, sodium sulphate was erroneously stated to melt at 843°. The correct value is 890°.
123	6*	for "C. PFLÜGER" read "E. PFLÜGER."
395	19	„ "this vol., ii, 395" read "this vol., ii, 404."

\* From bottom.



**I. A. R. I. 75.**

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